CAPACITIVE RF SHEATHS

ION TRANSIT TIME EFFECTS
COLLISIONLESS RF SHEATH REGIMES

- Recall capacitive sheath dynamics

- Ion velocity in sheath \( v_i = (2eV_s/M)^{1/2} \)

- Sheath thickness \( s_m \) from Child law [p. 76]

\[
e n_s u_B = 0.83 \epsilon_0 \left( \frac{2e}{M} \right)^{1/2} \frac{V_s^{3/2}}{s_m^2}
\]

- Ion transit time \( \tau_i = 3s_m/v_i \propto V_s^{1/4}/n_s^{1/2} \)

- RF period \( \tau_{rf} = 2\pi/\omega \)

- Two rf sheath regimes depending on the ordering of \( \tau_i \) and \( \tau_{rf} \)
LONG ION TRANSIT TIME

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

- Ion transit time \( \tau_i = 3s_m/v_i \ll \text{rf period } \tau_{\text{rf}} = 2\pi/\omega \) (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 \( 0 \lesssim \mathcal{E} \lesssim 2V_s \)
- Example: \( \bar{V}_s \sim 100 \text{ V}, n_s = 2 \times 10^{11} \text{ cm}^{-3}, f = 2 \text{ MHz} \)
  \[ \implies s_m = 0.43 \text{ mm}, \tau_i = 0.12 \tau_{\text{rf}} \]
- 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
  Steady ion current  Like pn junction diode
  
  \[ I_a(t) = en_s u_B A_a - \frac{1}{4} en_s \bar{v}_e A_a e^{-V_a(t)/T_e} \]  
  \[ I_b(t) = en_s u_B A_b - \frac{1}{4} en_s \bar{v}_e A_b e^{-V_b(t)/T_e} \]
  
  [p. 48]
• $I(t)$ 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
  $\implies V_a = V(t), \ V_b = 0$, 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 $\overline{V}_{bias}$ builds up across the blocking capacitor $C_B$ if $A_b \neq A_a$

• The voltage across the discharge is then [p. 120]

\[
V(t) = V_{rf} \sin \omega t + \overline{V}_{bias}
\]

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

\[
\overline{V}_{bias} = V_{rf} \sin \left( \frac{\pi}{2} \frac{A_b - A_a}{A_b + A_a} \right)
\]

• $\overline{V}_{bias} = 0$ for symmetric case $A_b = A_a$

• $\overline{V}_{bias} \to V_{rf}$ for highly asymmetric case $A_b \gg A_a$
FINITE FLOATING POTENTIAL

- In the limit \( A_b \gg A_a \), we see that
  \[
  \overline{V}_{\text{bias}} \to V_{\text{rf}}, \quad V_{\text{amax}} \to 2V_{\text{rf}}, \quad V_{b0} \to 0
  \]

- 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
  \[
  V_{b0} \approx 4.7 \, T_e
  \]
The sheath capacitors carry a small displacement current.

For an analytic treatment, see Kawamura et al, Plasma Sources Sci. Technol. 8, R45 (1999).

SMALL BUT FINITE ION TRANSIT TIME

- 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

- $g_i(\mathcal{E}) = \text{energy distribution}$ 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 $\frac{\omega}{2\pi}(t, t + dt) = \text{fraction of ions bombarding the substrate}$ 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

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

- The sum is over all phases $\omega t_j$ 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 $\tau_{rf}$

$$E(\omega t) \approx V_s(\omega t) \text{ and } \Gamma_i(\omega t_0) \approx n_s u_B = \text{const}$$

\[ V_s(t) - \]

Slow sheath motion

Fast ions

- Consider highly asymmetric case with $A_a \ll A_b \implies V_{bias} = V_{rf}$

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

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

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

$$dE/d(\omega t) = V_{rf}[1 - (E/V_{rf} - 1)^2]^{1/2}$$
EXAMPLE CALCULATION OF IED (CONT’D)

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

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

- The ion energy distribution is broad ($0 < \mathcal{E} < 2V_{rf}$) and independent of ion mass
**GENERAL CASE OF SHORT ION TRANSIT TIME**

- Ion transit time $\tau_i \ll$ rf period $\tau_{rf}$
  \[ \Rightarrow \mathcal{E}(\omega t) \approx V_s(\omega t) \text{ and } \Gamma_i(\omega t_0) \approx n_su_B = \text{const} \]

- Consider general asymmetric case with $A_a < A_b \Rightarrow \overline{V}_{\text{bias}}$ [p. 121]
  \[ \mathcal{E}(\omega t) = V_s(\omega t) = V_{rf} \sin \omega t + \overline{V}_{\text{bias}} \]

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

---

**Diagram:**
- Voltage profiles
- Energy distribution $g_i(\mathcal{E})$
- Powered (bottom)
LONG ION TRANSIT TIME

- Ion transit time $\tau_i \gg$ rf period $\tau_{rf}$
  \[ \Rightarrow \Gamma_i(\omega t_0) \approx n_s u_B = \text{const} \]

- Sheath voltage approximately sinusoidal with $\bar{V}_s \approx 0.83 \tilde{V}_s$ [p. 76]
  \[ V_s(\omega t) = \tilde{V}_s \sin \omega t + \bar{V}_s \]

- Ions “see” mostly the average sheath voltage $\bar{V}_s$ with a small time-varying perturbation $\Delta E$
  \[ E(\omega t) = \bar{V}_s + \Delta E(\omega t) \]

- Ion energy distribution is narrow and centered about $\bar{V}_s$
• Calculation of \( \frac{dE}{d(\omega t)} \) is rather complicated and yields (Benoit-Cattin and Bernard, 1968)

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

where

\[
\Delta E = \frac{4}{\pi} \frac{\tau_{rf}}{\tau_i} \bar{V}_s
\]

• This is a bi-modal distribution with two peaks

\[
E = \bar{V}_s \pm \Delta E/2
\]

• Because [p. 116]

\[
\tau_i = \frac{3s_m}{v_i} = 3s_m \sqrt{\frac{M}{2e\bar{V}_s}}
\]

there is an ion mass dependence

\[
\Delta E \propto \frac{1}{\sqrt{M}}
\]
ENERGY SPREAD $\Delta \varepsilon_i$ VERSUS $\tau_{rf}/\tau_i$

- Theory
- PIC Simulations

Conventional capacitive discharge

- Long $\tau_i$
  - Low density
  - High frequency

- Short $\tau_i$
  - High density
  - Low frequency

RF bias on high density plasma tool

$\frac{\Delta \varepsilon_i}{2 \bar{V}_s}$

Graph showing the relationship between $\Delta \varepsilon_i$ and $\tau_{rf}/\tau_i$ with data points and theoretical line.
• Erö (1958) showed the effect of rf modulation on IED’s

Energy spectrum has characteristic bi-modal shape

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), H$_2$O$^+$ (mass 18) and H$_3^+$ (mass 3)
  (Coburn and Kay, 1972)

• Capacitive discharge, CF$_4$ at 3 mTorr (Note $\Delta E \propto 1/\sqrt{M}$)
  (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

![Diagram of plasma and sheath](image)

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

\[ I(t) = I_0 \sin (2\pi f_0 t) \]
SIMULATIONS OF COLLISIONAL IED (CONT’D)

Ion Acceleration in the Sheath

IED on the Wafer

Peaks
SUMMARY OF ION ENERGY DISTRIBUTIONS (IED’S)

- IED’s are bi-modal (two peaks) in collisionless sheaths

- \( \tau_i \gg \tau_{rf} \implies \) Displacement current mainly flows in sheath
  Narrow IED centered around dc sheath potential \( V_s \)
  \[ \Delta \mathcal{E} \propto \frac{\tau_{rf}}{\tau_i} \propto \frac{1}{\sqrt{M}} \]

- \( \tau_i \ll \tau_{rf} \implies \) Conduction currents mainly flow in sheath
  Broad IED
  \[ 4.7 T_e < \mathcal{E} < \tilde{V}_{rf} + V_{bias} \]

- 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
  
  \( J = L + S; \quad (|L - S|, \ldots , L + S) \)
  
  \( \mathcal{E} = \mathcal{E}(L, S, J); \quad 2J + 1 \text{ states} \)
  
  Weak dependence of \( \mathcal{E} \) on \( J \) (“fine structure”)

- Electronic configurations
  
  Hydrogen: \( 1s \quad (^2S_{1/2}) \)
  
  Oxygen: \( 1s^22s^22p^4 \quad (^3P_2) \)
  
  Argon: \( 1s^22s^22p^63s^23p^6 \quad (^1S_0) \)
  
  Metastable argon: \( 1s^22s^22p^63s^23p^54s \quad (^3P_0, \; ^3P_2) \)
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
  \[ \implies \text{electric dipole radiation} \]

• 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 \( \tau_{\text{rad}} \sim 10^{-10} \text{ ns} \)

• Electric dipole radiation forbidden
  \[ \implies \text{metastable state} \]

• Examples: \( \text{Ar}(4s \, ^3P_0), \text{Ar}(4s \, ^3P_2) \)
ARGON ENERGY LEVELS

Ground state ($l=1$)

Metastable

$3p^6$ ($-15.76$ V)

$1S_0$ ($-15.76$)

$3p_0$ ($-4.037$) Metastable

$3p_1$ ($-4.136$)

$3p_2$ ($-4.211$) Metastable

$1P_1$ ($-3.932$)

$1P_1$ ($-2.487$)

$3P_0$ ($-2.432$)

$3P_2$ ($-2.457$)

$3P_1$ ($-2.477$)

$3P_0$ ($-2.487$)

$3P_1$ ($-2.507$)

$3D_2$ ($-2.588$)

$3D_1$ ($-2.607$)

$3D_2$ ($-2.665$)

$3D_3$ ($-2.684$)

$3S_1$ ($-2.853$)

$1S_0$ ($-2.280$)

$3P_1$ ($-2.432$)

$3P_2$ ($-2.457$)

$1P_1$ ($-2.477$)

$3P_0$ ($-2.487$)

$1D_2$ ($-2.588$)

$3D_1$ ($-2.607$)

$3D_2$ ($-2.665$)

$3D_3$ ($-2.684$)

$3S_1$ ($-2.853$)

Energy (volts)

0

$2P_{1/2} (Ar^+) \text{ ionization limit}$

$2P_{3/2} (Ar^+) \text{ ionization limit}$

$3P_1$ ($-2.477$)

$3P_2$ ($-2.457$)

$1P_1$ ($-2.477$)

$3P_0$ ($-2.487$)

$1D_2$ ($-2.588$)

$3D_1$ ($-2.607$)

$3D_2$ ($-2.665$)

$3D_3$ ($-2.684$)

$3S_1$ ($-2.853$)

$1S_0$ ($-2.280$)

$3P_1$ ($-2.432$)

$3P_2$ ($-2.457$)

$1P_1$ ($-2.477$)

$3P_0$ ($-2.487$)

$1D_2$ ($-2.588$)

$3D_1$ ($-2.607$)

$3D_2$ ($-2.665$)

$3D_3$ ($-2.684$)

$3S_1$ ($-2.853$)

$1S_0$ ($-2.280$)

$3P_1$ ($-2.432$)

$3P_2$ ($-2.457$)

$1P_1$ ($-2.477$)

$3P_0$ ($-2.487$)

$1D_2$ ($-2.588$)

$3D_1$ ($-2.607$)

$3D_2$ ($-2.665$)

$3D_3$ ($-2.684$)

$3S_1$ ($-2.853$)

$1S_0$ ($-2.280$)

$3P_1$ ($-2.432$)

$3P_2$ ($-2.457$)

$1P_1$ ($-2.477$)

$3P_0$ ($-2.487$)

$1D_2$ ($-2.588$)

$3D_1$ ($-2.607$)

$3D_2$ ($-2.665$)

$3D_3$ ($-2.684$)

$3S_1$ ($-2.853$)

$1S_0$ ($-2.280$)

$3P_1$ ($-2.432$)

$3P_2$ ($-2.457$)

$1P_1$ ($-2.477$)

$3P_0$ ($-2.487$)

$1D_2$ ($-2.588$)

$3D_1$ ($-2.607$)

$3D_2$ ($-2.665$)

$3D_3$ ($-2.684$)

$3S_1$ ($-2.853$)
• 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

\[ e \mathcal{E}_v = \hbar \omega_{vib} (v + \frac{1}{2}), \]
\[ v = 0, 1, 2, \ldots \]
MOLECULAR STATES

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

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

- For homonuclear molecules, $\Lambda_g$ and $\Lambda_u$ 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)
Most excited molecular states can radiate a photon and make a transition to a lower energy state

\[ \rightarrow \text{electric dipole radiation} \]

Selection rules for electric dipole radiation

\[
\begin{align*}
\Delta \Lambda &= 0, \pm 1 \\
\Delta S &= 0
\end{align*}
\]

\[
\Sigma^+ \rightarrow \Sigma^+ \text{ and } \Sigma^- \rightarrow \Sigma^- \\
g \rightarrow u \text{ and } u \rightarrow g
\]

Radiation lifetime \(\tau_{\text{rad}} \sim 10^{-100} \text{ ns}\)

Electric dipole radiation forbidden \(\Rightarrow\) 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** \(E_{\text{aff}}\) of the neutral atom or molecule \((A)\).

• Negative atomic and molecular ions \((A^-)\) are stable if \(E_{\text{aff}} > 0\). Typically \(E_{\text{aff}} \sim 0.5-3.5\) 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
COLLISION PRINCIPLES

• Two kinds of collisions
  — Electron collisions with atoms and molecules
    \[ e + A \rightarrow \text{products} \]
  — Heavy particle collisions with atoms and molecules
    \[ A + B \rightarrow \text{products} \]
    \[ A^+ + B \rightarrow \text{products} \]
    \[ A^- + B \rightarrow \text{products} \]

• By Newton’s laws, two bodies cannot elastically collide to form one body
  \[ e + A \not\rightarrow A^- \]
  \[ A + B \not\rightarrow AB \]

• Two bodies can collide to form one body if the internal energy increases
  \[ e + A \rightarrow A^{-*} \]
  \[ A + B \rightarrow AB^* \]
• Frank-Condon principle
  Nuclear positions are fixed during an electronic transition
• Due to the ordering of timescales for an electron collision
  \[ \frac{2a_0}{v_e} \ll \tau_{\text{vib}} \sim \tau_{\text{diss}} \ll \tau_{\text{rad}} \]
  \( a_0 \) = radius of atom or molecule; \( v_e \) = speed of incoming electron

• Dissociation
  \[ e + AB \rightarrow A + B + e \]
• Excitation
  \[ e + AB \rightarrow AB^* + e \]
• Ionization
  \[ e + AB \rightarrow AB^+ + 2e \]
• 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**
  \[ e + O_2 \rightarrow O_2^- \text{(unstable)} \rightarrow e + O_2 \quad (99\%) \]
  \[ \rightarrow O + O^- \quad (1\%) \]

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**
  \[ e + O_2 \rightarrow O_2^- \text{(unstable)} \rightarrow e + O_2 \quad (99\%) \]
  \[ \rightarrow O + O^- \quad (1\%) \]

- **Polar dissociation**
  \[ e + O_2 \rightarrow O^+ + O^- + e \]
  Non-resonant, high threshold energy
VIBRATIONAL AND ROTATIONAL EXCITATIONS

- Mechanism is often
  
  \[ e + AB(v = 0) \rightarrow AB^- \text{ (unstable)} \]
  
  \[ AB^- \rightarrow AB(v > 0) + e \]

ELECTRON COLLISIONAL ENERGY LOSSES

- Ionization
  Electronic excitation
  Elastic scattering
  Dissociation
  Vibrational excitation
  Rotational excitation
  etc.

- Electron collisional energy lost per electron-ion pair created, \( E_c \), is 2–10 times larger for molecules than for atoms [p. 40]
HEAVY PARTICLE COLLISIONS

• Ordering of timescales [p. 153]

\[
\frac{2a_0}{v_e} \ll \frac{2a_0}{v_i} \sim \tau_{\text{vib}} \ll \tau_{\text{rad}}
\]

\[v_i = \text{speed of incoming ion or neutral}\]

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

• Examples

\[A + B \rightarrow A^+ + B + e\] heavy particle ionization (very small)

(AB and AB\(^+\) curves do not cross or nearly touch)

\[A + B \rightarrow A^* + B\] heavy particle excitation (very small)

\[A^+ + B \rightarrow A^+ + B\] elastic scattering (large)

\[A^+ + A \rightarrow A + A^+\] resonant charge transfer (large)
NONRESONANT CHARGE TRANSFER

• Example of nitrogen and oxygen atoms
  \[ \text{N}^+ + \text{O} \rightarrow \text{N} + \text{O}^+ \] no threshold
  \[ \text{O}^+ + \text{N} \rightarrow \text{O} + \text{N}^+ \] 0.92 V threshold

• Example of oxygen atoms and molecules
  \[ \text{O}^+ + \text{O}_2 \rightarrow \text{O} + \text{O}_2^+ \] no threshold
  \[ \text{O}_2^+ + \text{O} \rightarrow \text{O}_2 + \text{O}^+ \] 1.4 V threshold

• Charge transfer makes ions of easier-to-ionize neutrals
NEGATIVE ION LOSS

- Positive-negative ion recombination (mutual neutralization)
  \[ A^- + B^+ \rightarrow A + B^* \]
  \[ \Rightarrow \text{large cross section; dominates negative ion destruction} \]

- Electron detachment
  \[ e + A^- \rightarrow A + 2e \]
  Like “ionization” of \( A^- \); can be important
REACTION RATES

- Consider reaction
  \[
  A + B \rightarrow \text{products}
  \]
  \[
  \frac{dn_A}{dt} = -K_{AB} n_An_B
  \]

- The rate coefficient is [p. 36]
  \[
  K_{AB}(T) = \langle \sigma_{AB}v_R \rangle_{\text{Maxwellian}}
  \]
  \[
  = \int_{0}^{\infty} f_m v_R \sigma_{AB}(v_R) 4\pi v_R^2 dv_R
  \]

- It often found to have an Arrhenius form
  \[
  K_{AB} = K_{AB0} e^{-\mathcal{E}_a/T}
  \]
  \[
  \mathcal{E}_a = \text{threshold or “activation” energy for the process}
  \]
  \[
  K_{AB0} = \text{“pre-exponential” factor (weakly depends on T)}
  \]
• Consider the reactions

\[
A + B \overset{K}{\underset{K'}{\rightleftharpoons}} C + D
\]

\(K\) has threshold or “activation” energy \(E_a\)

• From quantum mechanics and time reversibility

\[
m_R^2 g_A g_B v_R^2 \sigma(v_R) = m'_R^2 g_C g_D v'_R^2 \sigma'(v'_R)
\]

where

\[
m_R = \frac{m_A m_B}{m_A + m_B}, \quad m'_R = \frac{m_C m_D}{m_C + m_D}
\]

\[
\frac{1}{2} m_R v_R^2 = \frac{1}{2} m'_R v'_R^2 + eE_a
\]

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

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

• The $\bar{g}$’s are statistical weights (mean number of occupied states)

$\bar{g}_e = 2; \quad \bar{g}_{\text{atom}} \sim 1-10; \quad \bar{g}_{\text{mol}} \sim 100-1000$

$\implies \bar{g}$’s are given by thermodynamics

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

• Example

\[
e + A \xleftarrow{K_{\text{ex}}} e + A^*
\]

$K_{\text{ex}}$ (threshold energy $\mathcal{E}_{\text{ex}}$) is easy to measure or calculate

$K_{\text{deexc}}$ 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
  - \( A + B \rightarrow C + D \) can be elementary if A and B collide to immediately form C and D
  - \( 3A + 2B \rightarrow C + 2D \) is elementary if 3 molecules of A and 2 molecules of B simultaneously collide (not likely!)

- Types of elementary reactions
  A \( \rightarrow \) products (unimolecular)
  A + B \( \rightarrow \) products (bimolecular)
  A + B + C \( \rightarrow \) products (usually not elementary at low pressure)

- But recall by Newton’s laws [p. 152], the reaction
  A + B \( \rightarrow \) C (bimolecular with one product)
  is prohibited unless internal energy is given to C
RATE COEFFICIENTS

• First order elementary reaction

\[ A \rightarrow \text{products} \]
\[ \frac{dn_A}{dt} = -K_1 n_A \]

Units of \( K_1 \) (or \( \nu_1 \)) are \([s^{-1}]\)

• Second order elementary reaction

\[ A + B \rightarrow \text{products} \]
\[ \frac{dn_A}{dt} = \frac{dn_B}{dt} = -K_2 n_A n_B \]

Units of \( K_2 \) are \([m^3/s]\)
• Consider as an example the reaction chain
\[
A \xrightarrow{K_A} B \xrightarrow{K_B} C
\]
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
The reaction $A + B \rightarrow AB$
can not conserve energy and momentum [p. 152, 165]

This reaction can proceed by the chain

$$A + B \xleftrightarrow{K_2}{K_{-1}} AB^* \xrightarrow{K_1} AB + \hbar \omega$$

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

$$\frac{dn_{AB}}{dt} = K_1 n_{AB^*} = \frac{K_1 K_2}{K_{-1} + K_1} n_A n_B$$

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

\[
A + S \xrightleftharpoons[K_d]{K_a} A:S
\]

- 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\(^{-1}\)
    ~ 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]

\[ \Gamma_{\text{ads}} = s\Gamma_A = s \cdot \frac{1}{4} n_{AS} \bar{v}_A \]

\[ s(\theta, T) = \text{sticking coefficient} \]

\[ \theta = \text{fraction of surface sites covered with absorbate} \]

\[ n_{AS} = \text{gas phase density of A near the surface} \]

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

- Langmuir kinetics

\[ s(\theta, T) = s_0(1 - \theta) \]

\[ s_0 = \text{zero-coverage sticking coefficient} \ (s_0 \sim 10^{-6} - 1) \]
DESORPTION

\[ A: S \xrightarrow{K_d} A + S \]

- Rate coefficient has Arrhenius form [p. 161]

\[ K_d = K_{d0} e^{-\mathcal{E}_{\text{desor}}/T} \]

where \( \mathcal{E}_{\text{desor}} = \mathcal{E}_{\text{chemi}} \) or \( \mathcal{E}_{\text{physi}} \)

- Pre-exponential factors are typically

\[
\begin{align*}
K_{d0} & \sim 10^{14} - 10^{16} \text{ s}^{-1} \quad \text{physisorption} \\
& \sim 10^{13} - 10^{15} \text{ s}^{-1} \quad \text{chemisorption}
\end{align*}
\]
ADSORPTION-DESORPTION KINETICS

• Consider the reactions

\[
\begin{array}{c}
A + S \xleftrightarrow{K_d} A: S \\
\end{array}
\]

• Adsorbed flux is [p. 172]

\[
\Gamma_{ads} = K_a n_{AS} n'_0 (1 - \theta)
\]

\( n'_0 \) = area density \((\text{m}^{-2})\) of adsorption sites

\( n_{AS} \) = the gas phase density at the surface

\[
K_a = s_0 \frac{1}{4} \bar{v}_A / n'_0 \quad [\text{m}^3/\text{s}] \quad \text{(adsorption rate coef)}
\]

• Desorbed flux is [p. 173]

\[
\Gamma_{desor} = K_d n'_0 \theta
\]

\[
K_d = K_{d0} e^{-\mathcal{E}_{desor}/T} \quad [\text{s}^{-1}] \quad \text{(desorption rate coef)}
\]
• Equate adsorption and desorption fluxes ($\Gamma_{ads} = \Gamma_{desor}$)

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

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

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

![Graph of Langmuir isotherm](image-url)
CHEMISTRY IN DISCHARGES

NEUTRAL FREE RADICALS
• Example of N\textsubscript{2} discharge with low fractional ionization (n\textsubscript{g} \approx n\textsubscript{N\textsubscript{2}}) and planar 1D geometry (l \ll R)

\[ P_{\text{abs}} = \pi R^2 \]

- Determine T\textsubscript{e}
  Ion particle balance is [p. 46]

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

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

\[ \frac{K_{iz}(T_e)}{u_B(T_e)} \approx \frac{2h_l}{n gl} \Rightarrow T_e \]
• Determine edge plasma density $n_{is}$
  Overall discharge power balance [p. 50] gives the plasma density at the sheath edge

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

• Determine central plasma density

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

• Determine ion flux to the surface

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

• Determine ion bombarding energy

$$\mathcal{E}_i = 5.2T_e$$
FREE RADICAL BALANCE

- For nitrogen
  \[ e + N_2 \xrightarrow{K_{\text{diss}}} 2N + e \]

- Assume low fractional dissociation and loss of N atoms only due to a vacuum pump \( S_p \) (m³/s)
  \[ Al \frac{dn_N}{dt} = Al 2K_{\text{diss}}n_g n_i - S_p n_{NS} = 0 \]

- Solve for free radical density at the surface
  \[ n_{NS} = K_{\text{diss}} \frac{2Aln_g}{S_p} n_i \]

- Use \( n_i \) [p. 178] to find
  \[ n_{NS} = K_{\text{diss}} \frac{2n_g l}{S_p} \frac{P_{\text{abs}}}{2e\varepsilon_T h_l u_B} \]
FREE RADICAL BALANCE (CONT’D)

• Flux of N atoms to the surface

\[ \Gamma_{NS} = \frac{1}{4} n_{NS} \bar{v}_N \]

where \( \bar{v}_N = (8kT_N/\pi M_N)^{1/2} \)

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

\[ \Gamma_{NS} \propto \frac{n_g P_{abs}}{S_p} \]

• The ion flux \( \Gamma_{is} = n_{is} u_B \) scales as

\[ \Gamma_{is} \propto P_{abs} \]

Neutral/ion flux ratio \( \propto n_g / S_p \), independent of power
LOADING EFFECT

- Consider recombination and/or reaction of N atoms on surfaces
  \[
  \begin{align*}
  N + \text{wall} & \xrightarrow{\gamma_{\text{rec}}} \frac{1}{2}N_2 \\
  N + \text{substrate} & \xrightarrow{\gamma_{\text{reac}}} \text{product}
  \end{align*}
  \]

- Pumping speed \( S_p \) in the expression for \( n_{NS} \) [p. 179] is replaced by
  \[
  S_p \rightarrow S_p + \gamma_{\text{rec}} \frac{1}{4} \bar{v}_N (2A - A_{\text{subs}}) + \gamma_{\text{reac}} \frac{1}{4} \bar{v}_N A_{\text{subs}}
  \]

  \( A_{\text{subs}} \) is the part of the substrate area reacting with N atoms

- \( n_{NS} \) (and \( \Gamma_{NS} \)) are reduced due to recombination and reaction losses

- Therefore etch and deposition rates now depend on the part of the substrate area \( A_{\text{subs}} \) exposed to the free radicals, a \textit{loading effect}.
CHEMISTRY IN DISCHARGES

NEGATIVE IONS
INTRODUCTION

• Most materials processes use gases containing O, Cl, F, or Br-atoms
  \[ \Rightarrow \text{copious production of negative ions} \]

• Negative ions tend to trap in the center of the discharge
  \[ \Rightarrow \text{volume production rate} = \text{volume loss rate (no wall losses)} \]

• 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]
  \[ 0 = e n_+ E - e T_i \nabla n_+ - M \nu_i \frac{n_+ u_+}{\Gamma_+} \]
  with \( \nu_i \) the ion-neutral collision frequency [p. 38]
- Solve to find drift-diffusion equation for flux
  \[ \Gamma_+ = -D_+ \nabla n_+ + n_+ \mu_+ E \]
  with diffusion coefficient \( D_+ = e T_i / M \nu_i \), mobility \( \mu_+ = e / M \nu_i \)
- Electrons and negative ions are Boltzmann [p. 19]
  \( n_e = n_{e0} e^{\Phi / T_e}, \quad n_- = n_{-0} e^{\Phi / T_i} \)
- Plasma must be quasineutral [p. 21]
  \( n_+ = n_- + n_e \)
- Solve to obtain Fick’s law with ambipolar diffusion coefficient \( D_{a+} \)
  \[ \Gamma_+ = -D_{a+} \nabla n_+ \]
Diffusion coefficient $D_{a+}$ depends on electronegativity $\alpha$ and ratio $\gamma$ of electron/ion temperature

$$\alpha \equiv \frac{n_-}{n_e}, \quad \gamma \equiv \frac{T_e}{T_i} \approx 50$$

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

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

<table>
<thead>
<tr>
<th>State</th>
<th>$\mathcal{E}_{\text{diss}}$ (V)</th>
<th>$\mathcal{E}_{\text{iz}}$ (V)</th>
<th>Lifetime (s)</th>
<th>$\alpha_p$ ($a_0^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O^-(2P)$</td>
<td>—</td>
<td>13.61</td>
<td>—</td>
<td>5.4</td>
</tr>
<tr>
<td>$O^+(2\Pi_g)$</td>
<td>—</td>
<td>1.463</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$O^*(1D)$</td>
<td>—</td>
<td>11.64</td>
<td>147.1</td>
<td>—</td>
</tr>
<tr>
<td>$O_2(3\Sigma_g^-)$</td>
<td>5.12</td>
<td>12.14</td>
<td>—</td>
<td>10.6</td>
</tr>
<tr>
<td>$O_2^+(2\Pi_g)$</td>
<td>6.59</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$O_2^-(2\Pi_g)$</td>
<td>4.06</td>
<td>0.44</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$O_2^*(1\Delta_g)$</td>
<td>4.14</td>
<td>11.16</td>
<td>2700</td>
<td>—</td>
</tr>
<tr>
<td>$O_3$</td>
<td>1.05</td>
<td>12.67</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$O_3^-$</td>
<td>1.69</td>
<td>2.10</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
### SECOND ORDER RATE COEFFICIENTS FOR OXYGEN

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient (cm³/s)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>e + O₂ momentum transfer</td>
<td>4.7E–8Tₑ⁰.⁵</td>
<td>a</td>
</tr>
<tr>
<td>2</td>
<td>e + O₂ → O⁻ + O</td>
<td>8.8E–11exp(–4.4/Tₑ)</td>
<td>b</td>
</tr>
<tr>
<td>3</td>
<td>e + O₂ → 2O + e</td>
<td>4.2E–9exp(–5.6/Tₑ)</td>
<td>d</td>
</tr>
<tr>
<td>4</td>
<td>e + O₂ → O²⁺ + 2e</td>
<td>9.0E–10Tₑ² exp(–12.6/Tₑ)</td>
<td>d</td>
</tr>
<tr>
<td>5</td>
<td>e + O⁻ → O + 2e</td>
<td>2.0E–7exp(–5.5/Tₑ)</td>
<td>b</td>
</tr>
<tr>
<td>6</td>
<td>e + O²⁺ → 2O</td>
<td>5.2E–9/Tₑ</td>
<td>k</td>
</tr>
<tr>
<td>7</td>
<td>O⁻ + O²⁺ → O + O₂</td>
<td>(0.96,2)E–7(300/T)⁰.⁵</td>
<td>e,k</td>
</tr>
<tr>
<td>8</td>
<td>O⁻ + O → O₂ + e</td>
<td>(1.4,5)E–10</td>
<td>e,k</td>
</tr>
<tr>
<td>9</td>
<td>O⁻ + O²⁺ → 3O</td>
<td>1E–7</td>
<td>k</td>
</tr>
</tbody>
</table>

**Addition of O⁺**

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient (cm³/s)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>e + O₂ → O⁻ + O⁺ + e</td>
<td>7.1E–11Tₑ⁰.⁵ exp(–17/Tₑ)</td>
<td>r</td>
</tr>
<tr>
<td>11</td>
<td>e + O₂ → O + O⁺ + 2e</td>
<td>5.3E–10Tₑ⁰.⁹ exp(–20/Tₑ)</td>
<td>b</td>
</tr>
<tr>
<td>12</td>
<td>e + O → O⁺ + 2e</td>
<td>9.0E–9Tₑ⁰.⁷ exp(–13.6/Tₑ)</td>
<td>d</td>
</tr>
<tr>
<td>13</td>
<td>O⁻ + O⁺ → 2O</td>
<td>(2.7,2)E–7(300/T)⁰.⁵</td>
<td>e,k</td>
</tr>
<tr>
<td>14</td>
<td>O⁺ + O₂ → O + O²⁺</td>
<td>2.0E–11(300/T)⁰.⁵</td>
<td>e</td>
</tr>
</tbody>
</table>
## SECOND ORDER RATE COEFFICIENTS FOR OXYGEN (CONT’D)

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient (cm$^3$/s)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>$e + O_2 \rightarrow O_2^* + e$; see note f below</td>
<td>$1.7 \times 10^{-9} \exp(-3.1/T_e)$</td>
<td>b</td>
</tr>
<tr>
<td>16</td>
<td>$e + O_2^* \rightarrow e + O_2$</td>
<td>$5.6 \times 10^{-9} \exp(-2.2/T_e)$</td>
<td>b</td>
</tr>
<tr>
<td>17</td>
<td>$O_2^* + O_2 \rightarrow 2O_2$</td>
<td>$2.2 \times 10^{-18} (T/300)^{0.8}$</td>
<td>ke</td>
</tr>
<tr>
<td>18</td>
<td>$O_2^* + O \rightarrow O_2 + O$</td>
<td>$(1.0,7) \times 10^{-16}$</td>
<td>e,k</td>
</tr>
</tbody>
</table>

**Addition of metastable $O_2^* (1\Delta_g)$**

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient (cm$^3$/s)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>$e + O_2 \rightarrow O + O^* + e$</td>
<td>$5.0 \times 10^{-8} \exp(-8.4/T_e)$</td>
<td>d</td>
</tr>
<tr>
<td>20</td>
<td>$e + O \rightarrow O^* + e$</td>
<td>$4.2 \times 10^{-9} \exp(-2.25/T_e)$</td>
<td>d</td>
</tr>
<tr>
<td>21</td>
<td>$e + O^* \rightarrow e + O$</td>
<td>$8 \times 10^{-9}$</td>
<td>d</td>
</tr>
<tr>
<td>22</td>
<td>$e + O^* \rightarrow O^+ + 2e$</td>
<td>$9.0 \times 10^{-9} T^{0.7} \exp(-11.6/T_e)$</td>
<td>d</td>
</tr>
<tr>
<td>23</td>
<td>$O^* + O \rightarrow 2O$</td>
<td>$8 \times 10^{-12}$</td>
<td>e</td>
</tr>
<tr>
<td>24</td>
<td>$O^* + O_2 \rightarrow O + O_2$</td>
<td>$(6.4,7.0) \times 10^{-12} \exp(67/T)$</td>
<td>k,e</td>
</tr>
<tr>
<td>25</td>
<td>$O^* + O_2 \rightarrow O + O_2^*$</td>
<td>$1.0 \times 10^{-12}$</td>
<td>e</td>
</tr>
</tbody>
</table>
SECOND ORDER RATE CONSTANTS FOR OXYGEN (CONT’D)

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient (cm³/s)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>$O^- + O_2 \rightarrow O_3 + e$</td>
<td>$5E^{-15}$</td>
<td>k</td>
</tr>
<tr>
<td>27</td>
<td>$e + O_3 \rightarrow O_2^- + O$</td>
<td>$1E^{-9}$</td>
<td>k</td>
</tr>
<tr>
<td>28</td>
<td>$O^- + O_2^* \rightarrow O_3 + e$</td>
<td>$3E^{-10}$</td>
<td>k</td>
</tr>
<tr>
<td>29</td>
<td>$O^- + O_2^\ast \rightarrow O_2^- + O$</td>
<td>$1E^{-10}$</td>
<td>k</td>
</tr>
<tr>
<td>30</td>
<td>$O_2^- + O_2^+ \rightarrow 2O_2$</td>
<td>$2E^{-7}(300/T)^{0.5}$</td>
<td>k</td>
</tr>
<tr>
<td>31</td>
<td>$O_2^- + O^+ \rightarrow O_2 + O$</td>
<td>$2E^{-7}(300/T)^{0.5}$</td>
<td>k</td>
</tr>
<tr>
<td>32</td>
<td>$O_3^+ + O_2 \rightarrow O_2 + O + O_2$</td>
<td>$7.3E^{-10}exp(-11400/T)$</td>
<td>e</td>
</tr>
</tbody>
</table>

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)
   c. Based on data of Lee et al (1993)
   d. Eliasson and Kogelschatz (1986)
   e. Based on data of Eliasson and Kogelschatz (1986)
   f. Reactions 1–4, 10–11 for $O_2^\ast$ have activation energies reduced by $\sim 1$ V
   g. Kossyi et al (1992)
   h. Based on Rapp and Briglia (1965)
### THIRD ORDER RATE COEFFICIENTS FOR OXYGEN

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Rate Coefficient (cm$^6$/s)</th>
<th>Source</th>
</tr>
</thead>
</table>

#### Reactions among e, O$_2$, O$_2^+$, and O$^-$

1. $e + e + O_2^+ \rightarrow e + O_2$  
   $1\text{E}–19(0.026/T_e)^{4.5}$  
   ke

2. $e + O_2^+ + O_2 \rightarrow O_2 + O_2$  
   $6\text{E}–27(0.026/T_e)^{1.5}$, $1\text{E}–26$  
   k,e

3. $e + O + O_2 \rightarrow O^- + O_2$  
   $1\text{E}–31$  
   ke

4. $O^- + O_2^+ + O_2 \rightarrow O + O_2 + O_2$  
   $2\text{E}–25(300/T)^{2.5}$  
   k

5. $O + O + O_2 \rightarrow O_2 + O_2$  
   $2.45\text{E}–31T^{0.63}$  
   k

6. $O + O + O \rightarrow O_2 + O$  
   $1.3\text{E}–32(300/T)\exp(-170/T)$  
   e

#### Addition of O$^+$

7. $e + e + O^+ \rightarrow e + O$  
   $1\text{E}–19(0.026/T_e)^{4.5}$  
   ke

8. $e + O^+ + O_2 \rightarrow O + O_2$  
   $6\text{E}–27(0.026/T_e)^{1.5}$, $1\text{E}–26$  
   k,e

9. $O^- + O^+ + O_2 \rightarrow O_2 + O_2$  
   $2\text{E}–25(300/T)^{2.5}$, $2\text{E}–25$  
   k,e

10. $O^- + O^+ + M \rightarrow O + O + M$  
    $2\text{E}–25(300/T)^{2.5}$  
    k

11. $O^+ + O + O_2 \rightarrow O_2^+ + O_2$  
    $1\text{E}–29$  
    ke

#### Addition of metastable O($^1D$)

12. $O + O^* + O_2 \rightarrow O_2 + O_2$  
    $9.9\text{E}–33$  
    e

#### Notes and references

$^1T_e$ 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

  \[ e + O_2 \rightarrow O_2^+ + 2e \]  (ionization)

  \[ e + O_2 \rightarrow O^- + O \]  (dissociative attachment)

  \[ O_2^+ + O^- \rightarrow O_2 + O \]  (recombination)

  \[ O_2^+ + O_2 \rightarrow O_2^+ + O_2 \]  (elastic scattering)

  \[ O_2^+ + O_2 \rightarrow O_2 + O_2^+ \]  (charge transfer)

  \[ O^- + O_2 \rightarrow O^- + O_2 \]  (elastic scattering)

\[ \{ \text{momentum transfer} \implies \nu_i \implies D_+ \text{ [p. 184]} \]
UNIFORM DENSITY MODEL

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

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

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

$$P_{\text{abs}} = e\mathcal{E_c} K_{iz} n_e n_g \mathcal{V} + \Gamma_+ A e(\mathcal{E_e} + \mathcal{E_i}) \quad \text{(vol.+surf. loss)}$$

- Quasi-neutrality [p. 21]

$$n_+ = n_- + n_e$$

- Electronegative discharge $\alpha \gtrsim 1$

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

where $d_{\text{eff}} =$ 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 ($P_{\text{abs}}$) and geometry ($\mathcal{V}, A,$ and $d_{\text{eff}}$).

 (the solution is messy and not particularly illuminating)
NEGATIVE ION BALANCE

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

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

<table>
<thead>
<tr>
<th>High pressure/low plasma density</th>
<th>high ( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low pressure/high plasma density</td>
<td>low ( \alpha )</td>
</tr>
</tbody>
</table>

- 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 $V = \pi R^2 l$
- Low fractional dissociation and ionization $\implies n_g = n_{O_2} = \text{const}$
- 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]
  \[ O \xrightarrow{\gamma_{\text{rec}}} \frac{1}{2} O_2 \text{ (on wall)} \]
  with loss flux
  \[ \Gamma_{O} = \gamma_{\text{rec}} \cdot \frac{1}{4} n_{O} \bar{v}_{O} \]
  with $\bar{v}_{O} = (8kT_{O}/\pi M_{O})^{1/2}$
Differential Equations for Oxygen

- Particle balance using volume reactions 1–9 [p. 189]
  \[
  \frac{dn_{O^+}}{dt} = \text{volume generation} - \text{volume losses } - \nu_{O^+}n_{O^+} \\
  \frac{dn_{O^-}}{dt} = \text{volume generation} - \text{volume losses } - \nu_{O^-}n_{O^-} \\
  \frac{dn_O}{dt} = \text{volume generation} - \text{volume losses } - \nu_O n_O \\
  \]
  \[\text{surface loss}\]

- Power balance [p. 50]
  \[
  \frac{d}{dt} \left( \frac{3}{2} e n_e T_e \right) = \frac{P_{\text{abs}}}{V} - e \mathcal{E}_c K_{iz} n_e n_{O^2} - e(\mathcal{E}_e + \mathcal{E}_i) \nu_{O^2} n_{O^2} \\
  \]

- Quasi-neutrality [p. 21] gives
  \[n_e = n_{O^+} - n_{O^-}\]
• Second order rate coefficients $K(T_e)$ given on [p. 189]
• First order rate coefficient $\nu_{O_2^+}$ for positive ion loss to walls [p. 197]

\[ \nu_{O_2^+} = \frac{D_{a+} A}{d_{\text{eff}}} \frac{A}{V} \]

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

\[ \frac{1}{d_{\text{eff}}^2} = (\pi \frac{l}{R})^2 + (\frac{2.405}{R})^2 \]

• First order rate coefficient $\nu_O$ for O-atom loss to walls [p. 197]

\[ \nu_O = \gamma_{\text{rec}} \frac{\bar{v}_O A}{4V} \]

• Solve using Matlab/Mathematica/etc differential equation solver
LOW PRESSURE SOLUTION

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

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

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

- 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
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]

\[ O(g) + C(s) \xrightarrow{K_a} C:O \] (O atom adsorption)

\[ C:O \xrightarrow{K_d} CO(g) \] (CO thermal desorption)

\[ \text{ion} + C:O \xrightarrow{Y_i K_i} CO(g) \] (CO ion-assisted desorption)

• Let \( n'_0 \) = active surface sites/m²

• Let \( \theta \) = fraction of surface sites covered with \( C:O \) bonds

\[ 1 - \theta \]

\[ \theta \]

C(s) \hspace{1cm} CO(s)
SURFACE COVERAGE

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

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

- \(n_{OS}\) is the O-atom density near the surface
  \(n_{is}\) 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 \(Y_i \approx Y_{i0} \sqrt{E_i - E_{thr}}\) (as for sputtering)

  \[
  \Rightarrow \theta = \frac{K_a n_{OS}}{K_a n_{OS} + K_d + Y_i K_i n_{is}}
  \]
ETCH RATES

• The flux of CO molecules leaving the surface is
  \[ \Gamma_{\text{CO}} = (K_d + Y_i K_i n_{\text{is}}) \theta n_0' \text{ [m}^{-2}\text{s}^{-1}] \]
  with \( n_0' \) = number of surface sites/m²

• The vertical etch rate is
  \[ E_v = \frac{\Gamma_{\text{CO}}}{n_C} \text{ [m/s]} \]
  where \( n_C \) is the carbon atom density of the substrate

• The vertical (ion-enhanced) etch rate is
  \[
  E_v = \frac{n_0'}{n_C} \frac{1}{1 + \frac{1}{K_d + Y_i K_i n_{\text{is}} + \frac{1}{K_a n_{\text{OS}}}}} 
  \]

• The horizontal (non ion-enhanced) etch rate is
  \[
  E_h = \frac{n_0'}{n_C} \frac{1}{\frac{1}{K_d} + \frac{1}{K_a n_{\text{OS}}}} 
  \]
NORMALIZED ETCH RATES

\[ Y_i K_i n_{is} = 5 K_d \]

- High O-atom flux ⇒ highest anisotropy \( E_v/E_h = 1 + Y_i K_i n_{is}/K_d \)
- 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 $Y_i K_i n_{is} \gg K_d$

\[
\frac{1}{E_v} = n_C \left( \frac{1}{\Gamma_{is}} \left( \frac{1}{Y_i K_i n_{is} n_0'} \right) + \frac{1}{\Gamma_{OS}} \left( \frac{1}{K_a n_{OS} n_0'} \right) \right)
\]

- 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
• Sputtering of carbon
  \[ \Gamma_C = \gamma_{\text{sput}} K_i n_{i\text{s}} n'_0 \]

• Associative and normal desorption of O atoms,
  \[ C : O \rightarrow C + O(g) \]
  \[ 2C : O \rightarrow 2C + O_2(g) \]

• Ion energy driven desorption of O atoms
  \[ \text{ions} + C : O \rightarrow C + O(g) \]

• Formation and desorption of CO\textsubscript{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 $T_{ox} = 2$–20 nm

- Gate oxide voltage drop $V_{ox} = V_p - V_s$
  - $V_p = \text{dc plasma potential (with respect to ground)}$
  - $V_s = \text{dc voltage drop across sheath}$

- Breakdown when electric field in oxide satisfies

$$E_{ox} = \frac{V_{ox}}{T_{ox}} \gtrsim E_{BD} \approx 10 \text{ MV/cm}$$
DAMAGE DUE TO GATE OXIDE CURRENT

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

\begin{align*}
V_p &
\begin{array}{c}
\text{Plasma sheath} \\
\text{Gate oxide} \\
\text{Silicon substrate}
\end{array}
\end{align*}

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

\[ I = J_i A_g - J_{e0} A_g \exp \left( -\frac{V_p - V_{ox}}{T_e} \right) \]

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]

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

- **Antenna ratio** (AR) = $A_g/A_{ox}$
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, the maximum current density is
  \[ J_{ox} = AR \cdot J_i \]
  \[ \implies \text{minimize antenna ratio} \]

- Thicker oxides \(\implies\) less gate oxide current.
DAMAGE FROM NONUNIFORM PLASMAS

- To eliminate damage, float the substrate during plasma processing
  $\Rightarrow$ 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

\[
V_p(r) = T_e \ln \frac{n_e(r)}{n_e(0)}
\]
**OPEN CIRCUIT VOLTAGE ACROSS THICK OXIDE**

![Diagram of open circuit voltage across thick oxide](image)

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

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

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

  $$V_f = \frac{T_e}{2} \ln \frac{M}{2\pi m} \sim 4.7 T_e$$

- A voltage $V_{oc} = V_{p2} - V_{p1}$ appears across the two gate oxides
- The voltage capacitively divides across the oxides depending on their thicknesses and areas
• Oxides nearly conducting $\implies$ gate potentials nearly equal

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

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

• $V_2 > V_f \implies$ net ion current is collected in center
• $V_1 < V_f \implies$ 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 → no damage**
• 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
• After a sufficient overetch, the polysilicon has been entirely cleared.

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

• Solutions to all these damage mechanisms

$\implies$ 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

- Fraction $\alpha_i$ of ions collected < fraction $\alpha_e$ of electrons collected
- Current flowing to the resist surface must vanish
  \[ I_r = \alpha_i I_i - \alpha_e I_e e^{-V_r/T_e} = 0 \]
- Solve for resist potential
  \[ V_r = V_f + T_e \ln \frac{\alpha_e}{\alpha_i} \]
  Since $\alpha_e > \alpha_i$, $V_r > V_f$
- Current collected by gate is that not collected by resist
  \[ I_{ox} = (1 - \alpha_i) I_i - (1 - \alpha_e) I_e e^{-V_r/T_e} \]
- Eliminate $V_r$ to obtain
  \[ I_{ox} = I_i \left(1 - \frac{\alpha_i}{\alpha_e}\right) \]

$\Rightarrow$ damage
DAMAGE DUE TO RF BIASING

- Sheath voltage $V_s$, currents $I_i$ and $I_e$, and charge collected $Q_{ox}$ versus time $t$
• The oscillating $Q_{\text{ox}}$ produces an oscillating voltage $V_{\text{ox}}$ across the gate oxide

• Cheung and Chang (1994) plot “charging voltage” $V_{\text{ox}}$ 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

\[ \rightarrow \text{damage} \]
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

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 $10^N_{\text{knobs}} \Rightarrow \text{“combinatorial explosion”}$

- Access “forbidden” steady-state discharge regimes

- Pulse rf power $\Rightarrow$ 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 $\Rightarrow$ atomic layer deposition and etching
Physical Processes in the Recovery of TR Tubes

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.
• Attaching gases soak up electrons fast
IDEAL RECTANGULAR POWER WAVEFORM

- Duty ratio \( \eta = \frac{\tau_{on}}{\tau} \)
- Pulsing frequency \( f = \frac{1}{\tau} \)
- \( P_{abs} \) 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 $P_{\text{max}} = 2000$ W, $\eta = 0.25$ ($P_{\text{abs}} = 500$ 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]

\[ \mathcal{V} \frac{dn_e}{dt} = K_{iz} n_e n_g \mathcal{V} - n_e u_B A_{\text{eff}} \]

\text{ionization} \quad \text{collisional} \quad \text{in volume} \quad \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]

Plasma energy

increase

collisional

energy loss

\[ P_{\text{abs}}(t) = \mathcal{V} \frac{d}{dt} \left( \frac{3}{2} en_e T_e \right) + \mathcal{V} en_e n_g \sum_i K_i \mathcal{E}_i \]

\[ + A_{\text{eff}} \left[ e \left( \frac{V_s}{2} + \frac{5}{2} T_e \right) n_e u_B \right] \]

\text{energy loss to wall}

- Solve to obtain \( n_e(t) \) and \( T_e(t) \)
Differential Equations

- Particle balance reduces to

\[
\frac{1}{n_e} \frac{dn_e}{dt} = \nu_{iz} - \nu_{\text{loss}}
\]

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

- Eliminating \( dn_e/dt \) in the energy balance equation

\[
\frac{1}{T_e} \frac{dT_e}{dt} = \frac{P_{\text{abs}}(t)}{W_e} - \left( \frac{2 \mathcal{E}_c}{3 T_e} + 1 \right) \nu_{iz} - \frac{2}{3 \left( \frac{V_s}{T_e} + 1 \right)} \nu_{\text{loss}}
\]

with \( W_e(t) = \frac{3}{2}en_e T_e \mathcal{V} \), \( \mathcal{E}_c(t) = \) collisional energy loss per e-i pair [p. 39–40], and \( V_s(t) = \) dc sheath voltage
PULSED POWER ON

• Just after pulse turn-on, \( n_e \) and \( T_e \) are initially low

\[
\frac{1}{n_e} \frac{dn_e}{dt} \approx \nu_{iz} \\
\frac{1}{T_e} \frac{dT_e}{dt} \approx \frac{P_{\text{max}}}{W_e} - \left( \frac{2 \mathcal{E}_c}{3 T_e} + 1 \right) \nu_{iz}
\]

• 2nd term on the RHS of the \( dT_e/dt \) equation is initially low
  \( \Rightarrow \) Phase 1 (fast increase in \( T_e \))

• Later during the on-time, \( \nu_{iz} \) increases and the two terms on the RHS of the \( dT_e/dt \) equation nearly balance
  \( \Rightarrow \) Phase 2 (\( T_e \) decays, \( n_e \) increases)
PULSED POWER OFF

- $T_e$ falls such that $\nu_{iz} \ll \nu_{loss}$
  
  $\frac{1}{n_e} \frac{dn_e}{dt} \approx -\nu_{loss}$

  $\frac{1}{T_e} \frac{dT_e}{dt} \approx -\frac{2}{3} \left( \frac{V_s}{T_e} + 1 \right) \nu_{loss}$

  $\approx 4$ for argon

- Hence $T_e$ decays $4 \times$ faster than $n_e$ for argon $\Rightarrow$ Phase 3

- Note IEDF for $O_2^+$ ions escaping radially to the walls, for a helicon pulsed discharge, 250 $\mu$s on, 125 $\mu$s off
**COMPARISON OF MEASUREMENTS AND MODEL**

- Argon ICP, $\bar{P}_{\text{abs}} = 51$ 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 $\overline{P}_{\text{abs}}$, the average plasma density for a pulsed discharge can be higher than for a cw discharge ⇒ higher etch / dep rates

- The average $T_e$ is low due to low $T_e$ in the afterglow ⇒ the loss frequency $\nu_{\text{loss}} \propto (eT_e/M)^{1/2}$ decreases ⇒ 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
• Neutral radical dynamics
\[ \frac{dn_{\text{Cl}}}{dt} = 2K_{\text{diss}} n_e n_{\text{Cl}_2} - \nu_{\text{rec,Cl}} n_{\text{Cl}} \]

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

• Negative ion dynamics at power turn-off
\[ \frac{dn_{\text{Cl}^-}}{dt} = K_{\text{att}} n_e n_{\text{Cl}_2} - K_{\text{rec}} n_{\text{Cl}^+} n_{\text{Cl}^-} \]

— Attachment rate increases due to decay of \( T_e \)
— Fast loss of \( n_e \) by attachment and to walls
— After 30-50 \( \mu s \), \( \text{Cl}^- \) ions can be lost to walls
PULSED POWER CHLORINE TCP

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

Experiment (Ahn et al, 1995)

Figure 10. The time variation of (a) electron density $n_e$ and (b) electron temperature $T_e$ for 100 $\mu$s 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 $\mu$s; 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)

SECOND GENERATION
(2 sources, single wafer, high density)
THIRD GENERATION — DIELECTRIC ETCH
(Multi-frequency, single wafer, moderate density)

- 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

\[ \sim V_h \quad + \quad \sim V_l \quad \sim V_h \quad + \quad \sim V_l \]
CONTROL OF PLASMA DENSITY

- Consider capacitive discharge with equal area electrodes
- For a single frequency source
  \[ \text{Electron power balance} \implies \text{plasma density } n \]  
  \[ n \propto P_e \]
- For stochastic heating (with \( V_{rf} = 2 \tilde{V}_s \))
  \( P_e = \text{power absorbed by electrons} \propto \omega^2 V_{rf} \)  
  \[ \implies n \propto \omega^2 V_{rf} \]
  (similar scaling for ohmic heating)
- For two frequencies with \( \omega_h^2 V_h \gg \omega_i^2 V_i \)
  
  \[
  \text{High frequency source controls plasma density (ion flux)}
  \]
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 \( V_l \gg V_h \)

Low frequency source controls ion energy

- Ideal dual frequency operating regime

\[ \frac{\omega_h^2}{\omega_l^2} \gg \frac{V_l}{V_h} \gg 1 \]
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?
- Stochastic heating increases with low frequency voltage $V_l$
COUPLING OF VOLTAGES

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

\[ \mathcal{E}_i \approx 0.41 \left( V_l + V_h \right) \]

• Modeling results give a cross term

\[ \mathcal{E}_i \approx 0.41 \left( V_l + V_h - \frac{2}{3} \frac{V_l V_h}{V_l + V_h} \right) \]

cross term

• 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
  ($\tau_i = \text{ion transit time across the sheath}$)

\[ \implies \text{low-pass filter} \]
ION ENERGY DISTRIBUTION (IED)

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

\[ \text{Sheath voltage } V_s(t) \] \[ \text{Voltage seen by ions } V_i(t) \] \[ |dV_i/dt|^{-1} \] \[ \text{IEDF} \]

1. Fourier transform
2. Apply filter \( \alpha(\omega) \)
3. Inverse Fourier transform
4. Voltage seen by ions \( V_i(t) \)

- 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

400V/64MHz
800V/3MHz

0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002

0
200
400
600
800
1000

Energy (eV)

IED (1/eV)

Analytical

PIC

400V/64MHz
800V/2MHz

0.015
0.01
0.005

0
200
400
600
800
1000

Energy (eV)

IED (1/eV)

Analytical

PIC

Gap=3 cm
p=30 mTorr
Collisionless ions

400V/64MHz
800V/8MHz
800V/2MHz

0.015
0.01
0.005

0
200
400
600
800
1000

Energy (eV)

IED (1/eV)

Analytical

PIC

258
LiebermanShortCourse15
HIGH FREQUENCY ELECTROMAGNETIC EFFECTS
STANDING WAVES AND SKIN EFFECTS

- High frequency and large area ⇒ standing wave effects

- High frequency ⇒ high density ⇒ skin effects

Consider only the high frequency source

\[ - V_h + \]

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*

![Surface Wave Mode Diagram]

- **Radial wavelength** for surface wave (low density limit)
  \[ \lambda \approx \frac{\lambda_0}{\sqrt{1 + d/s}} \sim \frac{\lambda_0}{3} \]
  with \( \lambda_0 = c/f \) the free space wavelength

- **Axial skin depth** for surface wave [p. 99]
  \[ \delta_p \sim \frac{c}{\omega_p} \]

- There are also *evanescent modes* leading to edge effects near \( r = R \)
STANDING WAVE EFFECTS — FIXED DENSITY $n_e$

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

13.56 MHz ($\lambda \approx 9–10 \text{ m}$)  
40.7 MHz ($\lambda \approx 3 \text{ m}$)

Small standing wave and skin effects

Large standing wave effect; center-high profile
EXPERIMENTAL RESULTS FOR STANDING WAVES

40×40 cm discharge
$p = 150 \text{ mTorr}$
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,
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)

SKIN EFFECTS — FIXED FREQUENCY $f$

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

$$n_e = 10^9 \text{ cm}^{-3} \ (\delta_p = 17 \text{ cm}) \quad n_e = 10^{10} \text{ cm}^{-3} \ (\delta_p = 5.3 \text{ cm})$$

Small standing wave and skin effects

Large skin effects; center-low profile
SKIN EFFECTS

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

\[
\delta_p \lesssim 0.45 \sqrt{dR}
\]

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

- $d$ = 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 \( \Gamma_e \approx \Gamma_i \approx \Gamma \)

\[ \implies \text{Fick’s law} \quad \Gamma = -D_a \nabla n \text{ with } D_a = kT_e/M\nu_i \]

- 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

\[ h_l \equiv \frac{n_s}{n_0} \approx 2 \left( \frac{T_e}{T_i} \right)^{1/2} \frac{\lambda_i}{l} \]
DIFFUSION REGIMES AND $h_1$ FACTOR

![Graph showing diffusion regimes and the $h_1$ factor.]

- Low pressure
- Intermediate pressure
- High pressure

$h_l = \frac{0.86}{(3 + l/2\lambda_i)^{1/2}}$

$h_l = 2 \left( \frac{T_e}{T_i} \right)^{1/2} \frac{\lambda_i}{l}$

$p d$ (Torr-cm)
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

\[ K_{iz} n_g \left( \frac{2}{\pi} \eta_0 \right) \pi R^2 l = 2\pi R^2 h l \eta_0 u_B \]

- Solve with $h l \approx 2(T_e/T_i)^{1/2} \lambda_i/l$ to obtain

\[ \frac{K_{iz}(T_e)}{T_e^{1/2} u_B(T_e)} = \frac{1}{n_g d_{\text{eff}}} \]

where

\[ d_{\text{eff}} = 0.16 T_i^{1/2} \frac{l^2}{\lambda_i} \quad (T_i \text{ in volts}) \]

is an effective plasma size

- Given $n_g$ and $d_{\text{eff}} \implies$ electron temperature $T_e$
- $T_e$ varies over a narrow range of 1–3 volts
HIGH PRESSURE $T_e$ IN ARGON

\[ T_e (V) \]

\[ n_e d_{\text{eff}} \text{ (m}^{-2} \text{)} \]

\[ 10^{19} \quad 10^{20} \quad 10^{21} \quad 10^{22} \quad 10^{23} \quad 10^{24} \]
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 \( T_e \approx 1.5 \) 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 \( \mathcal{E}_e = 2T_e \approx 3 \) V and \( \mathcal{E}_i \approx 5.2T_e \approx 7.8 \) 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 \( J_{il} = e\lambda l n_0 u_B \approx 1.0 \) 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: $J_{rf} = 2.56 \text{ A/m}^2$ 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 $l/\lambda_i \rightarrow 2s_m/\lambda_i$ $\Rightarrow h_l$ is larger
HIGH PRESSURE OHMIC HEATING
(Kawamura et al, PoP 123505, 2014)

- Example of 700 mTorr, 2.56 A/m², 13.56 MHz, $\gamma_e = 0.1$

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

- 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
HIGH PRESSURE OHMIC HEATING (CONT’D)

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

\[
S_{\text{ohm}} = 1.73 \frac{m}{2e} \epsilon_0 \omega^2 (T_e \bar{V}_s)^{1/2} \nu_m h_l \left[ l + 2 s_m \left( \frac{1}{\pi} \ln \frac{2}{h_l} - 1 \right) \right]
\]

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

\[
S_{\text{ohm,sh}} = 0.24 \frac{m}{2e} \epsilon_0 \omega^2 \nu_m s_m \bar{V}_s
\]

- Stochastic heating in a single sheath:

\[
S_{\text{stoc}} = 0.92 \frac{m}{2e} \epsilon_0 \omega^2 \bar{v}_e \bar{V}_s
\]

with \( \bar{v}_e = (8eT_e/\pi m)^{1/2} \) the mean electron speed
### COLLISIONAL CHILD LAW

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

\[
\bar{J}_i = e n_s u_B = 0.82 \epsilon_0 \left( \frac{2e}{m} \right)^{1/2} \frac{V_s^{3/2}}{s_{m0}^2}
\]

is replaced by the collisional law (sheath width $s_m$)

\[
\bar{J}_i = e n_s u_B = 1.68 \epsilon_0 \left( \frac{2e}{m} \right)^{1/2} \frac{V_s^{3/2} \lambda_i^{1/2}}{s_m^{5/2}}
\]

- For the same $\bar{J}_i$ and $V_s$

\[
s_m = 1.33 \lambda_i^{1/5} s_{m0}^{4/5}
\]

Since $\lambda_i \ll s_{m0}$, the collisional sheath is typically 2–3 × thinner than the collisionless sheath.
The average ion bombarding energy is reduced below $V_s$ because energy is lost during charge transfer and elastic collisions in the sheath, creating fast neutrals

$$\mathcal{E}_i = \frac{1}{2} M_i u_i^2 \approx 0.62 \frac{\lambda_i}{s_m} V_s$$

However, the total energy (ions + fast neutrals) lost per ion transiting the sheath is still $V_s$
\[
\begin{align*}
\bar{V}_s &= 0.78 \tilde{V}_s, \quad \mathcal{E}_i = 0.62 \frac{\lambda_i}{s_m} \bar{V}_s \\
\bar{J}_i &= e n_s u_B = 1.68 \epsilon_0 \left( \frac{2e}{M} \right)^{1/2} \frac{V_s^{3/2}}{s_m^{5/2}} \lambda_i^{1/2} \\
\tilde{I}_{rf} &= 1.52 j \omega \frac{\epsilon_0 A}{s_m} \tilde{V}_s \\
P_{sh} &= \frac{m}{2e} \epsilon_0 \omega^2 (0.24 \nu_m s_m + 0.92 \bar{v}_e) \tilde{V}_s A \\
P_{ohm} &= 1.73 \frac{m}{2e} \epsilon_0 \omega^2 (Te \tilde{V}_s)^{1/2} \nu_m h_l \left[ l + 2 s_m \left( \frac{1}{\pi} \ln \frac{2}{h_l} - 1 \right) \right] A
\end{align*}
\]
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 \( V_{rf} = 300 \) 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, \( d_{eff} = d/2h_l = 5 \) cm [p. 46]
- With \( n_gd_{eff} \approx 1.65 \times 10^{21} \) m\(^{-2}\), the \( T_e \) versus \( n_gd_{eff} \) figure [p. 47] yields \( T_e \approx 1.7 \) 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]
- \( E_c \) versus \( T_e \) figure [p. 40] yields \( E_c \approx 187 \) V and \( E_c + 2T_e \approx 191 \) V
- Use the \( K_{el} \) versus \( T_e \) figure [p. 37] to find \( \nu_m \approx K_{el}n_g \approx 1.23 \times 10^9 \) s\(^{-1}\)
EXAMPLE (CONT’D)

- Evaluate bulk and sheath electron heating [p. 283]
  \[ P_{\text{ohm}} \approx 0.10 \tilde{V}_s^{1/2} \quad [\text{W}] \]
  \[ P_{\text{sh}} \approx 0.042 \tilde{V}_s \quad [\text{W}] \]
- Use \( \tilde{V}_s \approx V_{\text{rf}}/2 = 150 \text{ V} \) in above to find \( P_{\text{ohm}} \approx 1.2 \text{ W} \) and \( P_{\text{sh}} \approx 6.3 \text{ W} \)
- Electron power balance [p. 84] yields \( n_s \approx 1.1 \times 10^{15} \text{ m}^{-3} \)
- Since \( h_l = 0.1 \), \( n_0 \approx 1.1 \times 10^{16} \text{ m}^{-3} \)
- DC sheath voltage \( \overline{V}_s \approx 0.78 \tilde{V}_s \approx 117 \text{ V} \) and \( \mathcal{E}_i \approx 0.11 \text{ V} \) [p. 283]
- \( \bar{J}_i = e n_s u_B \approx 0.36 \text{ A/m}^2 \) [p. 283]
- \( J_{\text{rf}} \approx 34 \text{ A/m}^2 \) [p. 283]
- Total power balance [p. 84] gives \( P_{\text{abs}} \approx 22 \text{ W} \)
- The Child law [p. 283] gives \( s_m \approx 0.33 \text{ cm} \)
- \( s_m \) reasonably close to the initial estimate \( \implies \) but could iterate using this new value of \( s_m \)
ALPHA-TO-GAMMA TRANSITION


University of California, Berkeley
ALPHA MODE AND GAMMA MODE

(Raizer, Schneider, Yatsenko, 1995)

- 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

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.
SECONDARY ELECTRON EMISSION

- Auger emission for ion bombarding energy $E_i \lesssim 1$ kV

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

$$\gamma \approx 0.016(E_{iz} - 2E_{\phi}), \text{ independent of } E_i$$

- $\gamma \sim 0.25$ for He$, 0.1$ for Ar$, 0.03$ for O$^+, N_2^+$
FIRST TOWNSEND COEFFICIENT $\alpha$

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

$$\alpha = A p e^{-B p/E}$$

<table>
<thead>
<tr>
<th>Gas</th>
<th>$A$ (cm$^{-1}$-Torr$^{-1}$)</th>
<th>$B$ (V-cm$^{-1}$-Torr$^{-1}$)</th>
<th>Range of $E/p$ (V-cm$^{-1}$-Torr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.8</td>
<td>77</td>
<td>30–250</td>
</tr>
<tr>
<td>Ar</td>
<td>11.5</td>
<td>176</td>
<td>100–600</td>
</tr>
<tr>
<td>Xe</td>
<td>24</td>
<td>330</td>
<td>200–800</td>
</tr>
<tr>
<td>H$_2$</td>
<td>4.8</td>
<td>136</td>
<td>15–600</td>
</tr>
<tr>
<td>N$_2$</td>
<td>11.8</td>
<td>325</td>
<td>100–600</td>
</tr>
<tr>
<td>O$_2$</td>
<td>6.5</td>
<td>190</td>
<td>50–130</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>17</td>
<td>300</td>
<td>150–1000</td>
</tr>
<tr>
<td>CF$_4$</td>
<td>11</td>
<td>213</td>
<td>25–200</td>
</tr>
</tbody>
</table>

- Hence an initial electron flux grows exponentially in space

$$\frac{d\Gamma_e}{dz} = \alpha \Gamma_e \quad \Rightarrow \quad \Gamma_e = \Gamma_{e0} e^{\alpha z}$$
SHEATH BREAKDOWN CONDITION

- Consider the ion balance for a sheath of width $s$

- Ion flux balance in the sheath
  \[ \Gamma_+(0) = \Gamma_+(s) + \gamma \Gamma_+(0) (e^{\alpha s} - 1) \]

- Townsend condition for sheath breakdown: $\Gamma_+(s) = 0$
  \[ \gamma (e^{\alpha s} - 1) = 1 \]

- Substitute for $\alpha$ [p. 289]
  \[ E_b = \frac{Bp}{\ln Aps - \ln[\ln(1 + 1/\gamma)]} \]

- Breakdown field $E_b$ depends on $p$, $s$, and weakly, on $\gamma$
• Put $E_b = V_b/s_m$, with $V_b$ the maximum sheath voltage and $s_m$ the maximum sheath width:

$$V_b = \frac{B p s_m}{\ln A p s_m - \ln[\ln(1 + 1/\gamma)]}$$

• $V_b$ has a minimum at some value of $p s_m$
• $V_b \to \infty$ for

$$p s_m \to A^{-1} \ln(1 + 1/\gamma)$$
ALPHA-GAMMA TRANSITION

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

293
LOW P VOLTAGE VS CURRENT MEASUREMENTS

(Godyak and Khanneh, 1986)

Fig. 4. (a)–(d) Evolution of discharge parameters $I$, $T_e$, $n_e$, and $E$, during transition of a discharge into $\gamma$ regime; $f = 3.2$ MHz, $p = 3$ torr. Dotted line is theory from (26), (29), and (30) using experimental data of function $F(V_e)$ 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 (○)

\[(\text{air, 30 Torr, 0.9 cm gap, from p. 293})\]
HYSTERESIS MEASUREMENTS

(Raizer, Schneider, Yatsenko, 1995)

![Graphs showing current-voltage and power-voltage characteristics](image)

**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 $\alpha \rightarrow \gamma$ transition due to increasing current and voltage. As the current in the $\gamma$-mode decreases, the current, prior to the reversal $\gamma \rightarrow \alpha$, drops below the end points of the dashed lines, producing a hysteresis [2.20].
SIMULTANEOUS ALPHA AND GAMMA MODES

- $\alpha$ and $\gamma$ modes can co-exist (e.g., dielectric coated electrodes)

**FIGURE 2.30**
Coexistence of a ‘subnormal’ $\gamma$-mode and an $\alpha$-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).
The $\gamma$ 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 $\gamma$ mode limitation (for argon, $ps_m < 0.21$ Torr-cm).

For higher pressures, the $\alpha$ 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/H₂ capacitive discharges are used
- Active (dangling bond) and passive sites (area density $n'_0$)

\[
\theta_p \quad \theta_a
\]

- $\text{SiH}_2$ can insert at active and passive sites ("bad" film)
- $\text{SiH}_3$ diffuses along surface and inserts into active sites ("good" film)
- $\text{SiH}_3^+$ bombardment creates active sites and removes H-atoms
- $\text{SiH}_4$ hydrogenates the surface, creating passive sites
SURFACE REACTIONS AND RATES

\[ \text{SiH}_3^+ + \theta_p \xrightarrow{K_i} \theta_a + Y_i \text{H}(g) \]
\[ \text{SiH}_2 + \theta_a \xrightarrow{K_2} \theta_a \]
\[ \text{SiH}_2 + \theta_p \xrightarrow{K_{2p}} \theta_p \]
\[ \text{SiH}_3 + \theta_a \xrightarrow{K_3} \theta_p \]
\[ \text{SiH}_4 + \theta_a \xrightarrow{K_4} \theta_p + \text{SiH}_3(g) \]

- \( Y_i \sim 5–10 \) 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 \( \text{SiH}_3 \) before desorption
STEADY STATE ACTIVE SITE FRACTION

- Ion bombardment creates active sites
- SiH$_3$ and SiH$_4$ adsorption destroy active sites

\[
\frac{d\theta_a}{dt} = Y_i K_i n_{is} (1 - \theta_a) - K_3 n_{3S} \theta_a - K_4 n_{4S} \theta_a = 0
\]

\[\Rightarrow \theta_a = \frac{Y_i K_i n_{is}}{Y_i K_i n_{is} + K_3 n_{3S} + K_4 n_{4S}}\]

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

\[\theta_a \approx \frac{Y_i K_i n_{is}}{K_4 n_{4S}}\]

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

\[\Rightarrow \theta_a \sim 10^{-2}\]
DEPOSITION RATE

• The deposition rate is due to SiH$_3$ at the active sites and SiH$_2$ adsorption at all sites

\[
D_{\text{Si}} = (K_3 n_{3\text{S}} \theta_a + K_2 n_{2\text{S}}) \frac{n'_0}{n_{\text{Si}}}
\]

• In typical silane deposition discharges $n_{3\text{S}}/n_{2\text{S}} \sim 10^2$

• Then for $\theta_a \sim 10^{-2}$ and $K_3 \sim \overline{MK}_2 \sim 10 K_2$, the first term ("good" film deposition) is about $10\times$ the second term ("bad" film deposition)

• The preceding picture is oversimplified; for example
  \[
  \text{H} + \theta_a \longrightarrow \theta_p
  \]
  \[
  \text{H} + \theta_p \longrightarrow \theta_a + \text{H}_2(\text{g})
  \]
  \[\Rightarrow\] three-site model (McCaughey and Kushner, 1989)
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: “$T = 0.026 \text{ V}$” should be “$T = 0.026 \text{ V}$”.
p. 29, line 6: “$a_x v d v_x / d t$” should be “$a_x = d v_x / d t$”.
p. 32, Eq. (2.3.14): remove “.” (period) from the equation.
p. 37, equation above Eq. (2.4.12): “$4 \pi g(W) \text{ dW}$” should be “$g(W) \text{ dW}$”.
p. 37, Eq. (2.4.12): “$v(W)$” should be “$4 \pi v(W)$”.
p. 75, line 3: “(3.4.6)” should be “(3.4.7)”.

p. 143, Eq. (5.2.38): “$\frac{v_i^2}{D}$” should be “$\frac{V_{ix}}{D}$”.
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): “$\frac{d n_i}{d x}$” should be “$n \frac{d u_i}{d x}$”.
p. 174, 3rd line from bottom: “$5 \times 10^{-8} \text{ s}$” should be “$4 \times 10^{-8} \text{ s}$”.
p. 177, line 12: “$E = d \Phi / d x$” should be “$E = -d \Phi / d x$”.
p. 195, 5th line of 2nd paragraph: “all to easy” should be “all too easy”.
p. 197, Eq. (6.6.36): “[1 + $\frac{(V_B - \Phi_p)^{1/2}}{T_e}$]^304” should be “[1 + $\frac{(V_B - \Phi_p)}{T_e}^{1/2}$]^304”.
p. 221, line 4: add a space between “gas,” and “to obtain”.
p. 221, 3rd line after Eq. (7.3.31): “μįΓ = μį” should be “μį = μįΓ”.
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 “~ aeff. An electron with energy E_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): “T_i n_e E + T_i n_− E” should be “n_e E/T_i + n_− E/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_diss n_e n_a0” should be “K_diss n_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 “2πe” (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 \(V_s = -V(t)\).
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_T, K_l, and K||" should be \("\kappa_\perp, \kappa_\times, \kappa_T, \kappa_l, and \kappa||\)” wherever they appear in the text and equations.
p. 529, Figure 13.22: \("z c/\omega_pe\)” should be \("k z c/\omega_pe\)”.
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): “$\vec{E}_a + \vec{E}_h$” should be “$\vec{E} = \vec{E}_a + \vec{E}_h$”.
p. 689, Eq. (18.2.3): “Re” should be “$\frac{1}{2} Re$”.
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): “$(1 - k \cdot \vec{v})/\omega$” should be “$(1 - k \cdot \vec{v}/\omega)$”.
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: “$\Phi_0$” 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”.

307
ABOUT THE INSTRUCTOR

Michael A. Lieberman is Professor in the Graduate School in the Department of Electrical Engineering 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 CF₄ Discharge