Plasma

Discharges, sputtering, ion-surface interaction, thin-film processing
General

- Plasma: region of a gas discharge containing equal numbers of negative and positive charges (e\(^{-}\), i\(^{+}\), i\(^{-}\)).
- Only small portion of the gas species is ionized.
- The energies of the charge carriers and neutrals are randomized by collisions and interactions.
- Different energy distributions for various species. It is however useful to assume that their kinetic energies have a Maxwell-Boltzmann distributions corresponding to some equivalent $T$.
- Plasmas can be characterized by $n_e$, $n_i$, $n$, and $T_e$, $T_i$, and $T_n$.
- For stability of the plasma, charge generation should replenish charge-carrier loss due to recombination and out-diffusion.

$n_{e,i} \sim <10^7 \text{ cm}^{-3}$ space plasma

$<10^{20} \text{ cm}^{-3}$ man-made plasma

Parameters of different plasmas.
Schematics of Plasma Systems

- DC and RF systems
- $P \sim 1 - 100$ mTorr

Schematics of simplified sputtering systems

Limited to el. conducting materials
- Insulating materials can be sputtered
- Effective ionization
Use in Microfabrication

- Deposition of thin films by sputtering, ion plating, PECVD.
- Removal of surface layers and films by sputter etching, reactive-ion etching, and resist stripping.
Townsend Discharge

- Physical mechanism
  - For a discharge to occur, there must initially be some free electrons in the gas.
  - Cosmic rays and natural radioactivity can give rise to a small number of electrons and ions in gases.
  - Such an electron is then accelerated towards anode by the applied electric field $E$.
  - If the electron gained sufficient energy before colliding with a neutral-gas atoms, a further ionization can occur: $e^{-} + A \rightarrow 2e^{-} + A^{+}$.
  - Now two electrons are again accelerated and can ionize two more atoms resulting in further charge multiplication.
  - Meanwhile ions drift to the cathode and can kick off more neutrals and secondary electrons from it.
  - Avalanche current leads to:

- Voltage breakdown
  - The distance $d$ between electrodes should be sufficiently large to allow the electrons gain enough energy for the ionization avalanches.
  - The electrodes should be sufficiently wide to prevent the loss of electrons.

\[
i = i_0 \frac{\exp(\alpha d)}{1 - \gamma_e [\exp(\alpha d) - 1]}
\]

\[
\alpha = \frac{1}{\lambda} \exp \left( - \frac{V_i}{eE \lambda} \right)
\]

$V_i$, ionization potential; $
\alpha$ - the Townsend ionization coeff., the probability of ionization per unit length occurring during electron-atom collisions.
Paschen’s Law

\[ i = i_0 \frac{\exp(\alpha d)}{1 - \gamma_e[\exp(\alpha d) - 1]} \]

\[ \alpha = \frac{1}{\lambda} \exp \left( -\frac{V_i}{eE \lambda} \right); \quad \lambda \sim \frac{1}{P} \]

Breakdown takes place when the current is infinite, i.e. \(1 - \gamma[\exp(\alpha d) - 1] = 0\)

\[ V_B = \frac{A \cdot Pd}{\ln(B \cdot Pd)} \]

Mean-free path is too short to allow electrons gain sufficient energy to ionize gas atoms.

Few e-atom collisions: yield is too low to sustain ionization.

Min at \(\sim \exp(B)/B\)
Zoo of Discharges

- **Townsend discharge**: discharges in a uniform electric field; $10^{-15} - 10^{-6}$ A/cm$^2$; effects of space charge are not dominant; discharge is maintained by photoelectric or thermionic electron emission from the cathode.

- **Corona discharge**: Townsend discharge in inhomogeneous electric field (point-to-plane geometry, for instance); space-charge effects are dominant close to the small electrode; electron-energy gain is insufficient for avalanching between the electrodes.

- **Glow discharge**: Brightly glowing positive column with no electric field inside + dark space separating the column from the anode and cathode; $P \sim 10^{-3} - 1$ Torr; $10^{-4} - 10^{-1}$ A/cm$^2$; space-charge effects are important. Used in microfabrication.

- **Arc discharge**: $>10$ A/cm; low applied voltages; discharge current is emitted from a few small spots on the cathode; the high current originates thermionically at the cathode; the emitting spot can be self heated by the discharge or externally.
Discharges:

- All in one diagram
Structure of a DC Glow Discharge

- Aston dark space: low energy $e^-$ and high energy $i^+$
- Cathode glow: de-excitation of $i^+ \rightarrow$ light emission
- Cathode dark space: $e^-$ start to impact-ionize $n$; most of the voltage drops here.
- Negative glow: interaction with secondary electrons, excitation-de-excitation events. For sputtering, place your substrate here!
- Faraday dark space:
- Positive column:
- Anode dark space: high energy $e^-$ and low energy $i^+$

A floating electrode put inside plasma will acquire negative charge due to the disparity in mass and energy between electrons and ions → both the anode and cathode will be at negative floating potential relative to the plasma.
Some Physics of Plasma

- Plasma species and their motion in $E$ and $B$

  - Electrons and ions have almost independent velocity distributions.
  - The degree of gas ionization $i = n_e (n_e + n_0) \sim 10^{-4}$ in glow discharges ($n_e \sim 10^{10}$ cm$^{-3}$).
  - Energy of electrons: $1$-$10$ eV $\rightarrow T_e = 10^4$ $-$ $10^5$ K.
  - Energy of neutrals: $T_n \sim 300$ K
  - $T_n \neq T_e \rightarrow$ plasma is in thermodynamically non-equilibrium state

$$J_e = -n_e \mu_e E - D_e \frac{dn_e}{dx}$$

$$J_i = n_i \mu_i E - D_i \frac{dn_i}{dx}$$

$$\mu_i = \frac{v_i}{E} \sim 10^2$ - $10^4$ cm$^2$ V$^{-1}$ (for 1 Torr and 273K)

Charge neutrality $\Rightarrow$

$$J_e = J_i = J; \quad n_e = n_i = n$$

$$E = \frac{(D_i - D_e) \ dn}{n(\mu_i + \mu_e) \ dx}$$

**An electric field develops because of the charge separation due to the difference in electron and ion diffusivities.**

$$\vec{F} = -q(\vec{E} + \vec{v} \times \vec{B})$$
The Debye length $\lambda_D$ is a measure of the size of a mobile electron cloud required to reduce the radial electric potential $V(r)$ around a positive ion placed into the plasma to $1/e$ of its initial value.

$$V(r) = \frac{q}{r} \exp \left( -\frac{r}{\lambda_D} \right)$$

$$\lambda_D = \sqrt{\frac{\varepsilon_0 kT}{n_i q^2}}$$

The electron plasma frequency is a measure of the time required to restore charge equilibrium.

$$\omega_e = \sqrt{\frac{q^2 n_e}{m_e \varepsilon_0}} \approx 10^4 \sqrt{n_e} \text{ Hz},$$

$n_e [\text{cm}^{-3}]$

The plasma is opaque for a radiation with $\omega < \omega_e$. 


AC Effects in Plasmas

- RF discharges are more efficient than DC ones in promoting ionization
- Reactors without interior electrodes: clean plasma
- Self-bias of the plasma

\[ m_e \frac{dx^2}{dt^2} = -qE_0 \sin(\omega t) \]

the maximum displacement:

\[ x_0 = \frac{qE_0}{m_e \omega^2} \]

the maximum energy:

\[ K_0 = \frac{(qE_0)^2}{2m_e \omega^2} \]

For Ar ionization energy is 15.7 eV →

\[ E_0 = 11.5 \text{ V/cm for 13.6 MHz} \]
Self-Bias in AC Plasma

DC self-bias and sheath formation due to the difference in electron- and ion mobilities.
Collisions in Plasmas

- Can be both elastic and inelastic

\[
\frac{\Delta U}{K_1} = \frac{m_2}{m_1 + m_2} \cos^2 \theta \approx 1 \quad \text{for } \theta \approx 0
\]

Conservation of both momentum and kinetic energy →

\[
\frac{K_2}{K_1} = \frac{4m_1m_2}{(m_1 + m_2)^2} \cos^2 \theta
\]

the energy-transfer function

Almost all of the electron's kinetic energy can be transferred to the heavier species in the inelastic collision

is very small if a light particle hits a heavy one
Ionization Cross-Section

- There is a threshold value to eject the weakest-bound electron.
- Then, $\sigma$ increases with electron energy because larger number of accessible electron levels in atom
- $\sigma$ decreases after that.

\[
\sigma_{\text{total}} \approx \frac{4\pi}{k^2} \sin^2 \delta_0 = 4\pi a^2 \left( \frac{\tan \frac{k'a}{k'}}{k'} - 1 \right)^2.
\]
# Plasma Chemistry

## Chemical Reactions in Plasmas

### A. Electron collisions

<table>
<thead>
<tr>
<th>Type</th>
<th>Generic reaction</th>
<th>Example reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization</td>
<td>$e^- + A \rightarrow A^+ + 2e^-$</td>
<td>$e^- + O \rightarrow O^+ + 2e^-$</td>
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<tr>
<td></td>
<td>$e^- + A_2 \rightarrow A_2^+ + 2e^-$</td>
<td>$e^- + O_2 \rightarrow O_2^+ + 2e^-$</td>
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<tr>
<td>Recombination</td>
<td>$e^- + A^+ \rightarrow A$</td>
<td>$e^- + O^+ \rightarrow O$</td>
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<tr>
<td>Attachment</td>
<td>$e^- + A \rightarrow A^-$</td>
<td>$e^- + F \rightarrow F^-$</td>
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<tr>
<td></td>
<td>$e^- + AB \rightarrow AB^-$</td>
<td>$e^- + SF_6 \rightarrow SF_6^-$</td>
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<tr>
<td>Excitation</td>
<td>$e^- + A_2 \rightarrow A_2^+ + e^-$</td>
<td>$e^- + O_2 \rightarrow O_2^+ + e^-$</td>
</tr>
<tr>
<td></td>
<td>$e^- + AB \rightarrow (AB)^+ + e^-$</td>
<td></td>
</tr>
<tr>
<td>Dissociation</td>
<td>$e^- + AB \rightarrow A^* + B^* + e^-$</td>
<td>$e^- + CF_4 \rightarrow CF_3^+ + F^* + e^-$</td>
</tr>
<tr>
<td>Dissociative ionization</td>
<td>$e^- + AB \rightarrow A + B^* + 2e^-$</td>
<td>$e^- + CF_4 \rightarrow F + CF_3^+ + 2e^-$</td>
</tr>
<tr>
<td>Dissociative attachment</td>
<td>$e^- + A_2 \rightarrow A^+ + A^- + e^-$</td>
<td>$e^- + N_2 \rightarrow N^+ + N^- + e^-$</td>
</tr>
</tbody>
</table>

### B. Atom–ion–molecule collisions

<table>
<thead>
<tr>
<th>Type</th>
<th>Generic reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetrical charge transfer</td>
<td>$A + A^+ \rightarrow A^+ + A$</td>
</tr>
<tr>
<td>Asymmetric charge transfer</td>
<td>$A + B^+ \rightarrow A^+ + B$</td>
</tr>
<tr>
<td>Metastable–neutral (Penning ionization)</td>
<td>$A^* + B \rightarrow B^* + A + e^-$</td>
</tr>
<tr>
<td>Metastable–metastable ionization</td>
<td>$A^* + B^* \rightarrow B + A^+ + e^-$</td>
</tr>
</tbody>
</table>
Physics of Sputtering

- Zoo of events

![Diagram showing various processes in sputtering]

Sputter Yields

Sputter yield $S$ is the number of sputtered atoms per incident particle.

0.1 ns; $T=3300K$; $P=10^5$ atm: vaporization rather than collisional mechanism.

- In sputtering of alloys, the composition in the deposited thin film is the same as in the target.
- Sputter yields are different for various elements and materials.
- Sputter yield can depend on crystallographic orientation of the single-crystalline target.

Energy

- Single knock-on
- Linear cascade
- Spike

Graph showing yield vs. angle of incidence and energy.
Modification of Thin Films By Ions

- **Structural modifications**

  Ion bombardment modifies:
  - Surface topography and roughness
  - Crystallography and texture
  - Grain structure: grain size and morphology
  - Defects and stresses
  - Film orientation on amorphous substrates (IBAD – HTS thin films on Ni substrates)

  Usually, ion bombardment results in *smoothing* and improved step coverage enhanced by re-sputtering, but ->

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Ion Implantation

Important technique primarily used to modify or alter the subsurface structure of deposited thin films. Doping.

- Doping levels can be controlled precisely because the beam current can be accurately measured as an electric current.
- Doping uniformity across a surface can be accurately controlled.
- The depth profile can be regulated by choice of the incidence-ion energy.
- It is a low-temperature process. Important in some cases when heating is unnecessary.
- Extreme purity of the dopant can be guaranteed by mass-spectrometric analysis of the ion beam
- Directed beam, little spread sideways.
- Dopants that are not soluble or diffusible can be introduced.

FIGURE 4.19. Ion-implanted technique for selective introduction of dopants into the silicon lattice.
Damage Profiles During Implantation

- Heavy ions (Sb, As) are stopped primarily by nuclear collisions; therefore they cause a great deal of atom displacements.
- Lighter ions (B, P) are stopped by electronic interactions.

Impurities diffuse by either a substitutional or an interstitial mechanism: the ion-bombardment damage should increase the diffusion.

\[ D \sim (\text{flux})^{0.5} \]

\[ 5 \times 10^{11} \text{ protons/cm}^2\text{s} \]
Channeling Effects

- Difficult to control accurately

Due to the channeling effect, the resulting layer is deeper inside from the surface.
Bipolar Device Fabrication

- High-dose implantation are used for buried layers, emitters, and base-contact doping
- Low-dose implants for base regions and resistors

Oxidation is needed to consume the Si in which the implanted layer originally resided.
Summary Ion Bombardment

The main benefits of using ion bombardments:

- Enhancement of adatom surface mobility.
- Stimulation of the film nucleation, growth and coalescence.
- Development of preferred crystal orientation.
- Lower substrate temperatures for the onset of epitaxy.
- Crystallization of amorphous films and amorphization of crystalline films.
- Increased film/substrate adhesion.
- Modification of the film stress.
- Stimulation of the film-surface reactivity.
Plasma Etching

- Sputter etching

- Chemical etching. Plasma makes reactant species: $\text{NF}_3 \rightarrow \text{F}^*$. Isotropic etching, not possible to etch thin grooves. The most selective (chemically).

- Accelerated ion-assisted etching. Vertical ions damage the surface which is then attacked chemically by neutrals. Highly anisotropic due to the directional nature of the damage.

- Reactive-ion etching. Ions themselves are taking part in the chemical reaction. Needs high-density plasmas.
Plasma-Etching Reactors
Temperature Rise of Films During Plasma Processing

This heats the thin film:

• Heat of condensation of atoms $\Delta H_c$ (energy/atom)
• Average kinetic energy of incident adatoms $E_k$
• Heating from bombarding neutrals and electrons with energy $E_p$

<table>
<thead>
<tr>
<th>Metal</th>
<th>Heat of condensation (eV/atom)</th>
<th>Kinetic energy of sputtered atoms (eV/atom)</th>
<th>Plasma (eV/atom)</th>
<th>Estimated flux (eV/atom)</th>
<th>Measured flux (eV/atom)</th>
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<tbody>
<tr>
<td>Al</td>
<td>3.33</td>
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</tr>
</tbody>
</table>

*From Ref. 40.*
Film Heating

The film properties can be affected (loss of oxygen in YBCO or other HTS thin films, for instance)

Photoresist can become hard baked after the plasma treatment. Difficult to remove afterwards.

Solution: reduce energy; reduce the continuous etching time (use pulses)

Power flux 250 mW/cm²;
ε is the surface radiation emissivity
Ionized Cluster Beam Deposition

T. Takagi, 1987

Atom clusters (100-10000) are formed at relatively high pressure (0.01-10 Torr).

The clusters are then charged and can be accelerated towards the substrate by applying high voltage.

At the substrate, the clusters either break apart releasing atoms or can be deposited intact (prospective for nano-fabrication!)
Plasma-Immersion Ion Implantation

Enhances hardness and wear corrosion resistance by altering surface chemistry. Nitrides, carbides and oxides can form firmly adhered to the host material.

A number of steels, Al and Ti alloys can be treated in this way.

2-300 kV