L2b: Fundamentals of Vacuum Science and Technology: Plasma Physics and Chemistry, Particle-Surface Interactions

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Outline

- Kinetic theory of gases
- Atom/Surface and Ion-Surface Interactions
- Plasma Physics and Chemistry
Bibliography


Kinetic theory of gases provides a microscopic picture of gas laws.

**Assumptions:**

- A gas consists of a large number of molecules;
- separations are large compared to molecule size
- Molecules move randomly with a distribution in velocities which remains constant
- Molecules obey Newton’s laws of motion.
- Elastic collisions between the molecules; no other forces otherwise.
Pressure of gas molecules

\[ n = \frac{N}{V} \]

\[ p = F/A \text{ units [N/m}^2\text{]} \text{ or [Pa]} \]

Momentum change in one collision – \( 2m v_x \)
Time between collisions - \( \frac{2L}{v_x} \); frequency \( \frac{v_x}{2L} \)
Force by one molecule – \( 2m v_x \frac{v_x}{2L} = m v_x^2/L \)
Force by N molecules – \( N m v_x^2/L \)
Pressure – \( p = N m v_x^2/L A = n m v_x^2 \)

However, the average kinetic energy in \( x \)
\[ E = \frac{1}{2} m v_x^2 = \frac{1}{2} kT \]

\[ p = n k T \]

\( N \) - number of molecules
\( V \) - volume (= \( L \times A \))
\( p \) - pressure
\( T \) - absolute temperature
\( m, v \) - mass and velocity of molecules
\( k \) - Boltzmann constant = \( 1.38 \times 10^{-23} \) [J/K]
Collisions and mean free path

\[ \sigma = \pi \, d^2 \]

Mean free path \( \approx \frac{\text{travelling distance}}{\text{number of collisions}} = \frac{v \, \Delta t}{n \, \pi \, d^2 \, v \, \Delta t} = \frac{1}{n \, \sigma} \]

More accurate expression:
(with relative motion of all gas molecules)

\[ \lambda = \frac{1}{\sqrt{2} \, n \, \sigma} \]
Speed & energy distribution of gas molecules

Maxwell-Boltzmann distribution

**Velocity**

\[ f(v) = 4\pi \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \exp\left(-\frac{m}{2kT}v^2\right) v^2 \]

**Energy**

\[ f(\varepsilon) = 2\pi \left( \frac{1}{\pi kT} \right)^{\frac{3}{2}} \exp\left(-\frac{\varepsilon}{kT}\right) \sqrt{\varepsilon} \]

Average: \( v_{av} = \sqrt{\frac{8kT}{m}} \)

Root-mean-square: \( v_{rms} = \sqrt{\frac{kT}{m}} \)

Most probable: \( v_{p} = \sqrt{\frac{2kT}{m}} \)

Maxwell speed distribution function (10^6 cm/s)

Maxwell energy distribution function (eV^-1)

Velocity (10^5 cm/s)

Energy (eV)

**H2 25 °C**

**25 ° C**

**1000 °C**
Useful formulas

Mean free path

\[ \lambda = \frac{1}{\sqrt{2} \ n \ \sigma} \]

Gas density

\[ n = \frac{p}{kT} \]

Impinging gas flux on the walls

\[ J = \frac{nv}{4} = \frac{p}{\sqrt{2\pi mkT}} \]
# Examples

<table>
<thead>
<tr>
<th></th>
<th>$\lambda$</th>
<th>$J\ (\text{cm}^{-2}\ \text{s}^{-1})$</th>
<th>$t_{\text{ML}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$25^\circ\text{C}$</td>
<td>$1000^\circ\text{C}$</td>
<td>$25^\circ\text{C}$</td>
</tr>
<tr>
<td>1 atm ($10^5$ Pa)</td>
<td>70 nm</td>
<td>300 nm</td>
<td>2.4 $\times 10^{23}$</td>
</tr>
<tr>
<td>1 Torr ($133$ Pa)</td>
<td>50 $\mu$m</td>
<td>200 $\mu$m</td>
<td>3.2 $\times 10^{20}$</td>
</tr>
<tr>
<td>1 mTorr (0.133)</td>
<td>5 cm</td>
<td>20 cm</td>
<td>3.2 $\times 10^{17}$</td>
</tr>
<tr>
<td>$10^{-6}$ Torr</td>
<td>50 m</td>
<td>200 m</td>
<td>3.2 $\times 10^{14}$</td>
</tr>
<tr>
<td>$10^{-11}$ Torr</td>
<td>5,000 km</td>
<td>20,000 km</td>
<td>3.2 $\times 10^9$</td>
</tr>
</tbody>
</table>

$\lambda$: mean free path of Ar  
$J$: flux of Ar atoms on sample surface  
$t_{\text{ML}}$: time to form a monolayer (ML) at sticking probability of 1
Adsorption

Incident atoms or molecules must lose energy to bond. Energy barriers may block transfer to stronger bonding structures.

Core repulsion

- Strong chemical bonding
- Weak chemical bonding
- van der Waals bonding

Energy barrier to strong bonding

Not all states shown may be present for a given system
Adsorption: Sticking Coefficient

Some gas species stick only where a reactive site is available. If the adsorbing species stays on this site a limited time a steady state partial coverage results.

Reflection or very weak adsorption occurs at previously covered sites ($\phi \sim 0$).

Even on an open site the probability $\phi$ is less than 1.0.
Desorption

Atoms may leave a surface alone or in groups.

Simple desorption is thermally activated and concentration independent.

$$r_{\text{des}} = C^n r_0 e^{-\Delta G/kT}$$

$\Delta G$: the desorption energy

$C$: adatom concentration

$k$: Boltzmann’s constant

$n$: the desorption reaction order

$T$: Temperature

$r_0$: the desorption attempt rate

Associative desorption involves multiple atoms and is concentration dependent.

Desorption from chemically different areas proceeds at different rates.
Surface Diffusion

Atoms move on simple surfaces by a series of jumps over energy barriers. The flux is given by Fick’s Law, \( J = -D \frac{dC}{dx} \).

The diffusivity, \( D \):

Diffusion over individual barriers is given by:

\[
D = D_0 e^{-\frac{\Delta E}{kT}}
\]

- \( D_0 \): an attempt frequency (constant)
- \( \Delta E \): the energy barrier for a given hop
- \( k \): Boltzmann’s constant
- \( T \): Temperature

Atoms spend the most time in the deepest energy minima.

Barrier height is modified around surface steps and impurities.
Erlich Barrier

Adatoms diffusing on an upper terrace require an additional energy (the Ehrlich barrier, $E_b$) to cross descending step edges. $E_s$ is the surface diffusion activation barrier. Note that adatoms that cross descending edges move into a deep trap ($E_f$) due to higher bond coordination.

The barrier asymmetry at step edges leads to a tendency for up-hill flux resulting in kinetic roughening.
Features of a clean substrate surface

- bunches of steps
- adatom
- surface vacancy
- terrace
- step
- kink
Transfer among nuclei; ripening deposition flux [cm$^{-2}$s$^{-1}$]

Nucleation and Growth

stable clusters

metastable clusters

adatom diffusion

surface vacancy

a step edge acts as an infinite size nucleus.
transfer among nuclei; ripening

Nucleation and Growth

The critical radius $r^*$

The nucleation energy barrier, $E^*$

Cluster Size (atoms)

Cluster Energy (Arbitrary Units)

-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0

surface energy

volume energy
Once nuclei have been formed these grow by collection of atoms and transfer of atoms between the nuclei, and coalesce by moving as a unit until two nuclei meet.

\[ \gamma_f \leq \gamma_s \quad \text{2D, island growth} \]

\[ \gamma_f > \gamma_s \quad \text{3D, island growth} \]

\( \gamma \): surface and interfacial energies
Growth modes

- **2-D Layer-by-Layer Growth (Frank-van der Merwe)**, e.g., Si/Si, TiN/MgO
- **3-D Island Growth (Volmer-Weber)**, e.g., Metals on SiO₂
- **Stranski-Krastanov**, e.g., In/Si, Ag/Si, Ge/Si
Growth processes controlling microstructure evolution

- condensation of atom, surface diffusion
- nucleation of isolated islands
- island growth
- impingement and coalescence of islands
- formation of polycrystalline islands and channels
- development of continuous film
- local epitaxy on grains&columns
- competitive column growth and grain coarsening
- (Renucleation)

Case of pure elemental materials
Zone Structure Models

Concept of Homologous Temperature: $\frac{T_{\text{substrate}}}{T_{\text{melting}}}$
(to account for differences in activation barriers for different materials)

SZMs systematically categorize self-organized structural evolution during PVD (similar or related diagrams can be formulated for CVD and electrodeposition) as a function of deposition parameters.

From an understanding of film formation follows the possibility for microstructural and nanostructural engineering in order to design a material for specific technological applications.

Plasma-based deposition processes

- Ion plating
- Activated reactive evaporation
- Cathodic arc deposition

- Bias sputter deposition
- Ion-beam assisted deposition
- Dual ion-beam sputtering
Sputter deposition

Basics:
- A voltage is applied across a rarified gas.
- Breakdown of the gas forms a glow discharge plasma.
- Positive ions from the plasma strike the negative electrode.
- Energy from the ions is transferred to target atoms.
- A few of these may escape from the target surface (they are sputtered).
- The sputtered atoms condense on the substrate forming a film.
Plasma is a partially ionized gas with nearly equal numbers of positive and negative charges. The gas is typically 1-10% ionized.

The cathode region is essential for discharge maintenance.
Ion surface interactions

Elastic Effects

- Sputtered Particles: $T^0, T^+, T^n$
- Reflected Particles: $I^0, I^+$

Positive ions are returned by the electric field

Inelastic Effects

- Negative Ions: $T^-, I^-$
- UV/visible photons
- X-rays

Accelerated by the field

Implanted Particles: $I^0$

Target

Figure after G.M. McCracken, Rep. Prog Phys. 28, 241 (1975).
Glow Discharge Maintenance

Secondary ion-electron yield

< 1 kV, electrons emitted from the conduction band of the target due to the potential energy of the ion
Glow Discharge Maintenance

Electron impact ionization

Figure after John A. Thornton and Alan S. Penfold, in *Thin Film Processes*, Ed. by John L. Vossen and Werner Kern (Academic Press, New York, 1978) p. 84.
Glow Discharge Maintenance

On the average, an secondary electron emitted from the cathode must acquire energy sufficient to produce a number of ions to release one further electron from the cathode.

\[ V_T = \frac{E_o}{\gamma_i \varepsilon_i \varepsilon_e} \]

Explain materials dependencies
Sheath width

Child-Langmuir formula

\[ d^2 = \frac{4\varepsilon_0}{9} \left( \frac{2e}{m} \right)^{1/2} \frac{V^{3/2}}{j} \]

for \( Ar^+ \rightarrow d^2 [m^2] = \frac{4 \times 8.854 \times 10^{-12}}{9} \left( \frac{2 \times 1.6 \times 10^{-19}}{40 \times 1.66 \times 10^{-27}} \right)^{1/2} \frac{V^{3/2} [V]}{j \left[ \frac{A}{m^2} \right]} \approx 8.64 \times 10^{-9} \frac{V^{3/2}}{j} \]
Plasma parameters

- Electron density & temperature: $n_e$, $T_e$
- Ion density & temperature: $n_i$, $T_i$
- Plasma potential: $V_{\text{plasma}}$

Assumptions

- Singly charged ions: $n_e \approx n_i$
- Cold ions: $T_i \ll T_e$

For film growth, we need to know:

- Ion flux $J_i$ and
- Ion energy $E_i \approx e(V_{\text{substrate}} - V_{\text{plasma}})$
Charge particle fluxes

From the kinetic theory:

\[ J_{i,e} = \frac{n_i, V_{i,e}}{4} = \frac{n_{i,e}}{4} \sqrt{\frac{8 k T_{i,e}}{\pi m_{i,e}}} = 0.4 n_{i,e} \sqrt{\frac{k T_{i,e}}{m_{i,e}}} \]

Ions at the edge of the sheath are accelerated to

\[ v_i \sim \sqrt{\frac{k T_e}{m_i}} \quad \Rightarrow \quad J_i = 0.6 n_i \sqrt{\frac{k T_e}{m_i}} \]

Note: \( J_i = f(T_e) \)
Idealized Probe Characteristics

\[ I_{\text{probe}} = I_i + I_e \]

\[ V_{\text{probe}} > V_{\text{plasma}} \]

\[ I_e = I_e^{\text{sat}} = eJ_e = 0.4en_e\sqrt{\frac{kT_e}{m_e}} \]

\[ I_i = 0 \]

\[ V_{\text{probe}} \leq V_{\text{plasma}} \]

\[ I_i = I_i^{\text{sat}} = eJ_i = 0.6en_e\sqrt{\frac{kT_e}{m_i}} \]

Electrons much lighter; for Ar\(^+\) the ratio is \(\sim 200\)
Small cylindrical probe

Does not disturb the discharge; good to measure $T_e$ and $V_{\text{plasma}}$, not $J_i$

\[ I_e = I_{\text{probe}} - I_i^{\text{sat}} = I_e^{\text{sat}} e^{\frac{V_{\text{probe}} - V_{\text{plasma}}}{kT_e}} \]

\[ \ln I_e = -\frac{V_{\text{probe}} - V_{\text{plasma}}}{kT_e} + \ln I_e^{\text{sat}} \]

\[ \Delta \ln I_e = -\frac{e\Delta V_{\text{probe}}}{kT_e} \Rightarrow kT_e = -\frac{e\Delta V_{\text{probe}}}{\Delta \ln I_e} \]
Effective current-collecting areas of probes

Effective Collecting Interface

Sheath

Probe
Flat Probe

- Good to directly measure ion flux; \[ I_{probe} = \frac{e J_{sat}^{ion}}{1 - \gamma} \]

\( \gamma \): Secondary electron emission coefficient correction of the order ~ 10%

- Big probe
  - Electron saturation disturbs the plasma (acts as an anode).
  - Tangent method cannot be used.

\[ V_{float} = I_e \]

\( T_e \) can be determined from the initial portion of the exponential rise of \( I_e \)

\[ V_{plasma} = V_{float} + \text{const.} \ T_e \]
Practical example

\[ d^2[cm] = 8.64 \times 10^{-6} \frac{V^{3/2}[V]}{j[mA/cm^2]} \]

\[ \lambda_{CE} = \frac{kT}{p[Pa]\sigma[m^2]\sqrt{2}} \]

\[ \sigma_{CE}^{Ar} = 4 \times 10^{-19} \left[ m^2 \right] \]

<table>
<thead>
<tr>
<th>Sputtering system</th>
<th>Voltage</th>
<th>Current density</th>
<th>Sheath width</th>
<th>( \lambda_{Ar} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diode p_{Ar} = 70 mTorr</td>
<td>target</td>
<td>3000 V</td>
<td>1 mA cm(^{-2})</td>
<td>12 mm</td>
</tr>
<tr>
<td></td>
<td>substrate</td>
<td>100 V</td>
<td>0.1 mA cm(^{-2})</td>
<td>3 mm</td>
</tr>
<tr>
<td>magnetron p_{Ar} = 3 mTorr</td>
<td>target</td>
<td>500 V</td>
<td>50 mA cm(^{-2})</td>
<td>(0.5 \text{ mm})</td>
</tr>
<tr>
<td></td>
<td>substrate</td>
<td>100 V</td>
<td>1 mA cm(^{-2})</td>
<td>(0.9 \text{ mm})</td>
</tr>
</tbody>
</table>

For magnetron sputtering \( \lambda_{Ar} > \text{sheath width} \rightarrow E_i \approx e(V_{\text{electrode}} - V_{\text{plasma}}) \)