Thin Film Deposition techniques

Sputtering

Sputtering Deposition

• Plasma Generation
• Sputtering
• Transportation of film materials
• Adhesion, nucleation and growth
• Film formation
Plasma

![Electron Temperature (eV)](image)

**Electron Density (cm⁻³)**

DC Discharge

![Voltage vs. Current](image)
DC glow discharge

Fig. 1 Voltage distribution in a dc glow discharge process.

Regions in Plasma
DC glow discharge

- Glow: atoms are excited by inelastic collisions and relax into their ground state by photon emission

**Cathode**
- emission of e\(^-\) (thermal, photoeffect, field emission), positive ions from the plasma, sputter cathode atoms

**Aston (1st) dark space...negative glow**
- e\(^-\) accelerate towards the anode and ionize gas atoms

**negative glow**
- maximum ionization rate

**Cathode (Crooke’s) dark space ... cathode glow**
- ions accelerate towards the cathode

- Substrate can be placed inside the negative glow and acts as anode
- Other parts of glow discharge do not appear

---

**Plasma Generation Parameters**

- Influencing process parameters:
  - Gas pressure \( p \)
  - High voltage \( V \)
  - Distance cathode - anode: \( d \)

- e\(^-\) must gain sufficiently high energy in order to ionize gas atoms
  - \( \rightarrow p \) not too high, \( V \) not too low
- e\(^-\) must find a gas atom for inelastic collision
  - \( \rightarrow p \) not too low

- Sufficient number of ions with sufficient energy must hit the target to induce secondary electron emission
  - \( \rightarrow p \) not too high

- Plasma ignition must be possible
  - \( \rightarrow d \) not too short

\[ pd \geq 40 \text{ Pa} \cdot \text{cm} \]

\[ p = 3-300 \text{ Pa} \quad V = 1...2 \text{ kV} \]
to achieve evaporation, binding energy must be supplied
a-thermal/ballistic energy transfer:
- bombardment by fast, heavy and non-reactive ions, ejection of atoms
- sputtering by noble gas ions
- ions are extracted from a plasma
- typical ion energies: 500eV...10keV
  (binding energies: 1-5eV)
- plasma control is essential
plasma: gas with significant fractions of ionized molecules and free electrons
target can be far away from plasma or part of a glow discharge
RF-MAGNETRON SPUTTERING

BILLIARD BALL MODEL OF SPUTTERING

- \( \text{In, O, Sn atoms} \)
- Neutral BS Argon
- 2\textsuperscript{nd} electron
- Radiation

\[ \text{Direction of momentum transfer} \]
BILLIARD BALL MODEL OF SPUTTERING

Prevents ignition of plasma between vacuum wall and cathode (d too short)
Sputtering Systems

Ion Beam Sputtering

Glow Discharge

Target=evaporant

Sputtering Yield: $Y(E, \theta)$

**Sputtering Yield:**

Number of atoms ejected per incident ion

$E_i$, Incident Energy (eV)

Smith 8.27/8.29
Sputtering Targets

<table>
<thead>
<tr>
<th>Materials</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Metallization for Integrated Circuit, Front Surface mirrors</td>
</tr>
<tr>
<td>Cr</td>
<td>Adhesion Layers, Resistor Films (with SRO Lithography), Master Blanks</td>
</tr>
<tr>
<td>Ge</td>
<td>Infrared Filter</td>
</tr>
<tr>
<td>Au</td>
<td>Contacts, Reflecting Films</td>
</tr>
<tr>
<td>Fe, Ni</td>
<td>Ferromagnetic Films</td>
</tr>
<tr>
<td>Pt, Pd</td>
<td>Contacts</td>
</tr>
<tr>
<td>Ag, Cu</td>
<td>Reflective Films, contacts</td>
</tr>
<tr>
<td>Ta</td>
<td>Thin film Capacitors</td>
</tr>
<tr>
<td>W</td>
<td>Contacts</td>
</tr>
<tr>
<td>Alloys</td>
<td></td>
</tr>
<tr>
<td>Al-Cu, Al-Si, Al-Cu-Si</td>
<td>Metallization for Integrated Circuit</td>
</tr>
<tr>
<td>Co-Pt, Co-Ni, Fe-Ti, Fe-Ni, Co-Ni-Cr</td>
<td>Ferromagnetic Films</td>
</tr>
<tr>
<td>Ni-Cr</td>
<td>Resistors</td>
</tr>
<tr>
<td>Ti-Al</td>
<td>Diffusion Resistors in Integrated Circuits</td>
</tr>
<tr>
<td>Gd-Co</td>
<td>Magnetic Bubble memory Devices</td>
</tr>
<tr>
<td>Oxides</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Insulation, Protective films for mirrors</td>
</tr>
<tr>
<td>Bi₂O₃, PbTiO₃</td>
<td>Thin Film Capacitors</td>
</tr>
<tr>
<td>CeO₂</td>
<td>Antireflection Coatings</td>
</tr>
<tr>
<td>In₂O₃, SnO₂</td>
<td>Transparent Conductors</td>
</tr>
<tr>
<td>LiNbO₃</td>
<td>Piezoelectric films</td>
</tr>
<tr>
<td>SiO</td>
<td>Insulation</td>
</tr>
<tr>
<td>SiO₂, Y₂O₃, ZrO₂, HfO₂, MgO</td>
<td>Dielectric Films for Multilayer coatings</td>
</tr>
<tr>
<td>Yttrium Aluminum oxide (YAG)</td>
<td>Magnetic Bubble memory Devices</td>
</tr>
<tr>
<td>Yttrium Iron Oxide (YIG)</td>
<td></td>
</tr>
<tr>
<td>Gd₂Ga₂O₇</td>
<td>Phosphorescent coating on special currency papers</td>
</tr>
<tr>
<td>Cu₂Ba₄Y₂O₇</td>
<td>High Temperature Superconductors</td>
</tr>
</tbody>
</table>
Suppose that a free argon ion is within a RF field of 5 V/cm amplitude, at 13.56 MHz.

i) Calculate its acceleration, velocity, and displacement due to the field, assuming that there are no collisions with other particles. The acceleration, velocity, and displacement of the ion will all be sinusoids of this frequency. We will calculate their amplitudes.

ii) The pressure is 10⁻² torr. Is the assumption of no collisions a good one? The mean free path at this pressure is on the order of 0.8 cm. This is much larger than the amplitude of the ion's displacement, so the assumption is valid.

iii) Will the temperature of the ion population be influenced by this field?

iv) Estimate the rms speed of an electron as it moves in response to the given field, again assuming no collisions, and estimate the effective temperature of the electron gas.
main reason for widespread use of sputter techniques:
sputtering allows for the deposition of films
having the same composition as the target source
(after a conditioning phase)
different target atoms have different sputter yields (preferential
sputtering)

→ surface composition ≠ bulk composition
(negligible solid-state diffusion at room temperature provided)
in contrast, melts homogenize readily

### Sputtering of Alloys

<table>
<thead>
<tr>
<th>binary alloy AB:</th>
<th>( n = n_A + n_B ) surface atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>composition (at-%):</td>
<td>( c_A = \frac{n_A}{n} ) ( c_B = \frac{n_B}{n} )</td>
</tr>
<tr>
<td>sputter yields:</td>
<td>( S_A, S_B )</td>
</tr>
</tbody>
</table>

initial ratio of sputtering rates

\[
\frac{\psi_A}{\psi_B} = \frac{S_A \cdot c_A}{S_B \cdot c_B}
\]

\( n'_A = n_A - n_A c_A S_A \)
\( n'_B = n_B - n_A c_A S_B \)
\( n' = n'_A + n'_B \)

surface composition change after \( n_g \) incident ions:

\[
\frac{c'_A}{c'_B} = \frac{c_A - n_A c_A S_A}{c_B - n_A c_B S_B} = \frac{c_A \left(1 - \frac{n_A S_A}{c_A}ight)}{c_B \left(1 - \frac{n_A S_B}{c_B}ight)}
\]

\( S_A < S_B \Rightarrow \left(1 - \frac{n_A S_A}{c_A}\right) > \left(1 - \frac{n_A S_B}{c_B}\right) \Rightarrow \frac{c'_A}{c'_B} > \frac{c_A \left(1 - \frac{n_A S_A}{c_A}\right)}{c_B \left(1 - \frac{n_A S_B}{c_B}\right)} \)

and

\[
\frac{\psi'_A}{\psi'_B} = \frac{S_A c'_A}{S_B c'_B} = \frac{S_A c_A \left(1 - \frac{n_A S_A}{c_A}\right)}{S_B c_B \left(1 - \frac{n_A S_B}{c_B}\right)} ctc.
\]
additional magnetic field traps electrons longer in the plasma region (Lorentz force)

→ higher sputter rate at lower pressure, higher film purity, less diffuse scattering of sputtered atoms, localization of plasma, erosion trench

Magnetron Sputtering

e.g. Permalloy target (Ni$_{40}$Fe$_{60}$), 1kV Ar$^+$ ions:

$S_{Ni}=2.2$, $S_{Fe}=1.3$, surface composition in the steady state is Ni$_{40.3}$Fe$_{59.7}$
Magnetron: confinement

B \hspace{2cm} E

\begin{itemize}
\item Target (cathode)
\item \(\text{Ar}^+\)
\end{itemize}

Cylindrical post magnetron and facing target

substrate holder

target rod

electron trajectory

(a) the Pulsed-DC facing target sputtering system
inert sputter gas is mixed with a reactive gas (N₂, H₂, O₂, S₂, CH₂, CH₄, ...) these molecules dissociate in the plasma and react with sputtered atoms to nitrides, hydrides, oxides, sulfides, carbides, etc. partial pressure ratio Ar/N₂ etc. determines stoichiometry

Reactive Sputtering

RF sputtering

comprehensive explanation is difficult (see Smith) some facts without further explanation:
• during a rf period electrons and ions accelerate towards the electrodes
• ion current µ electrode area
• electron current is independent of electrode area
• small electrode (target) collects net negative charge
• target develops a negative bias voltage
• capacitance C prevents de-charging and target remains negative
• positive ions hit target only, no sputtering of container walls
### Property Modification by Ion Bombardment (I)

<table>
<thead>
<tr>
<th>Film materials</th>
<th>Ion</th>
<th>Property Modified</th>
<th>Ion energy (eV)</th>
<th>Ion/atom Arrival Rate ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>Ar⁺</td>
<td>stress, adhesion</td>
<td>65-3000</td>
<td>2×10⁻⁴ to 10⁻¹</td>
</tr>
<tr>
<td>Nb</td>
<td>Ar⁺</td>
<td>stress</td>
<td>100-400</td>
<td>3×10⁻²</td>
</tr>
<tr>
<td>Cr</td>
<td>Ar⁺, Xe⁺</td>
<td>stress</td>
<td>3,400-11,500</td>
<td>8×10⁻³ to 4×10⁻²</td>
</tr>
<tr>
<td>Cr</td>
<td>Ar⁺</td>
<td>stress</td>
<td>200-800</td>
<td>~7×10⁻³ to 2×10⁻²</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Ar⁺</td>
<td>step</td>
<td>500</td>
<td>0.3</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Ar⁺</td>
<td>step, coverage</td>
<td>~1-80</td>
<td>~4.0</td>
</tr>
<tr>
<td>AIN</td>
<td>N⁺²</td>
<td>preferred Orientation</td>
<td>300-500</td>
<td>0.96 to 1.5</td>
</tr>
<tr>
<td>Au</td>
<td>Ar⁺</td>
<td>Coverage at 50 Å thickness</td>
<td>400</td>
<td>0.1</td>
</tr>
</tbody>
</table>

### Property Modification by Ion Bombardment (II)

<table>
<thead>
<tr>
<th>Film materials</th>
<th>Ion</th>
<th>Property Modified</th>
<th>Ion energy (eV)</th>
<th>Ion/atom Arrival Rate ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>GdCoMo</td>
<td>Ar⁺</td>
<td>magnetic Anisotropy</td>
<td>~1-150</td>
<td>~0.1</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu⁺</td>
<td>improved Epitaxy</td>
<td>50-400</td>
<td>10²</td>
</tr>
<tr>
<td>BN</td>
<td>(B-N-H)⁺</td>
<td>Cubic</td>
<td>200-1,000</td>
<td>~1.0</td>
</tr>
<tr>
<td>ZrO₂, SiO₂, TiO₂</td>
<td>Ar⁺, O⁺²</td>
<td>Refractive index armor-&gt; cryst</td>
<td>600</td>
<td>2.5×10⁻⁴ to 10³</td>
</tr>
<tr>
<td>SiO₂, TiO₂</td>
<td>O⁺²</td>
<td>refractive index</td>
<td>300</td>
<td>0.12</td>
</tr>
<tr>
<td>SiO₂, TiO₂</td>
<td>O⁺²</td>
<td>Optical transmission</td>
<td>30-500</td>
<td>0.05 to 0.25</td>
</tr>
<tr>
<td>Cu, Ni on Fe</td>
<td>N⁺², Ar⁺</td>
<td>Adhesion</td>
<td>50,000</td>
<td>10⁻²</td>
</tr>
<tr>
<td></td>
<td>Ar⁺</td>
<td>Hardness</td>
<td>10,000-20,000</td>
<td>~0.25</td>
</tr>
</tbody>
</table>