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Film Deposition

Lecture notes from

Physical Vapor Deposition by R. Darling

http://www.engr.washington.edu/~cam/PROCESSES/physicalvapdeppdf.html
OUTLINE

• Thin film deposition methods
• Evaporation
  – Physics and simple model
• Electrochemical deposition
METHODS

• Conductors - metal films, polysilicon
• Insulators – dielectrics SiO₂
• Semiconductors – GaAs …

• Chemical Vapor Deposition (CVD)
  – Low Pressure (LPCVD)
  – Plasma Enhanced (PECVD)

• Epitaxy
  – Vapor Phase (VPE)
  – Liquid Phase (LPE)
  – Molecular Beam (MBE)

• Evaporation
  – Thermal (Filament)
  – Electron-beam
  – Flash

• Sputtering

• Electrochemical Deposition
Chemical Vapor Deposition (CVD)

Three common susceptors for chemical vapor deposition:
(a) horizontal, (b) pancake, and (c) barrel susceptors.

Figure 8.1 (p. 145 May and Sze)
Molecular Beam Epitaxy

Figure 8.5 (p. 149) May and Sze
Arrangement of the sources and substrate in a conventional molecular beam epitaxy (MBE) system. (Courtesy of M. B. Panish, Bell Laboratories, Lucent Technologies).
Spattering

May and Sze Figure 8.18 (p. 168)
(a) Standard sputtering. (b) Long-throw sputtering. (c) Sputtering with a collimator.
EVAPORATION
Evaporation System Requirements

• Vacuum:
  – Need $10^{-6}$ torr for medium quality films.
  – Can be accomplished in UHV down to $10^{-9}$ torr.

• Cooling water:
  – Hearth
  – Thickness monitor
  – Bell jar

• Mechanical shutter:
  – Evaporation rate is set by temperature of source, but this cannot be turned on and off rapidly. A mechanical shutter allows evaporant flux to be rapidly modulated.

• Electrical power:
  – Either high current or high voltage, typically 1-10 kW.
Evaporation Support Materials

• Refractory metals:
  – Tungsten (W); MP = 3380°C, P* = 10^{-2} torr at 3230°C
  – Tantalum (Ta); MP = 3000°C, P* = 10^{-2} torr at 3060°C
  – Molybdenum (Mo); MP = 2620°C, P* = 10^{-2} torr at 2530°C

• Refractory ceramics:
  – Graphitic Carbon (C); MP = 3700°C, P* = 10^{-2} torr at 2600°C
  – Alumina (\text{Al}_2\text{O}_3); MP = 2030°C, P* = 10^{-2} torr at 1900°C
  – Boron nitride (BN); MP = 2500°C, P* = 10^{-2} torr at 1600°C

• Engineering considerations:
  – Thermal conductivity
  – Thermal expansion
  – Electrical conductivity
  – Wettability and reactivity
Resistance Heated Evaporation

- Simple, robust, and in widespread use.
- Can only achieve temperatures of about 1800°C.
- Use W, Ta, or Mo filaments to heat evaporation source.
- Typical filament currents are 200-300 Amperes.
- Exposes substrates to visible and IR radiation.
- Typical deposition rates are 1-20 Angstroms/second.
- Common evaporant materials:
  - Au, Ag, Al, Sn, Cr, Sb, Ge, In, Mg, Ga
  - CdS, PbS, CdSe, NaCl, KCl, AgCl, MgF₂, CaF₂, PbCl₂
Resistance Heated Evaporation Sources

- wire hairpin
- wire helix
- wire basket
- alumina crucible with wire basket
- foil dimple boat
- alumina coated foil dimple boat
- foil trough
- chromium coated tungsten rod
- alumina crucible in tantalum box
Electron Beam Heated Evaporation - 1

• More complex, but extremely versatile.
• Can achieve temperatures in excess of 3000°C.
• Use evaporation cones or crucibles in a copper hearth.
• Typical emission voltage is 8-10 kV.
• Exposes substrates to secondary electron radiation.
  – X-rays can also be generated by high voltage electron beam.
• Typical deposition rates are 10-100 Angstroms/second.
• Common evaporant materials:
  – Everything a resistance heated evaporator will accommodate, plus:
  – Ni, Pt, Ir, Rh, Ti, V, Zr, W, Ta, Mo
  – Al₂O₃, SiO, SiO₂, SnO₂, TiO₂, ZrO₂
Electron Beam Heated Evaporation Source

- 4-pocket rotary copper hearth (0 V)
- Pyrolytic graphite hearth liner
- Evaporation cones of material
- Recirculating cooling water
- 270 degree bent electron beam
- Magnetic field
- Cathode filament (-10,000 V)
- Beam forming aperture

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Electron Beam Heated Evaporation - 2

• 270° bent beam electron gun is most preferred:
  – Filament is out of direct exposure from evaporant flux.
  – Magnetic field can be used for beam focusing.
  – Magnetic field can be used for beam positioning.
  – Additional lateral magnetic field can be used to produce X-Y sweep.

• Sweeping or rastering of the evaporant source is useful for:
  – Allows a larger evaporant surface area for higher deposition rates.
  – Allows initial charge to be “soaked” or preheated.
  – Allows evaporant source to be more fully utilized.

• Multiple pocket rotary hearth is also preferred:
  – Allows sequential deposition of layers with a single pump-down.
  – Allows larger evaporation sources to be used.
PHYSICS AND MODELS

(First order effects)
Physical Vapor Deposition

- Gas Phase
- Transport
- Evaporation
- Condensed Phase (solid or liquid)
- Condensation
- Gas Phase (usually solid)
Equilibrium Vapor Pressure

- $P^*$ is the partial pressure of a gas in equilibrium with its condensed phase at a given temperature $T$.
  - No net transfer of material from one state to the other.
- For a given material, $P^*$ is only a function of $T$.
  - But the dependence of $P^*$ on $T$ is rather complicated.
Evaporation Rates - 1

- \( P^* \) is the equilibrium vapor pressure of the evaporant at \( T \).
- \( P \) is the ambient hydrostatic pressure acting upon the evaporant in the condensed phase.
- Heinrich Hertz found experimentally that the evaporation rate was proportional to \((P^* - P)\).
  - This is consistent with kinetic theory in which the impingement rates are proportional to pressure.
  - Hertz also found that the evaporation rate could not be increased by supplying more heat unless the equilibrium vapor pressure was also increased by this action.
  - Thus, there is a maximum evaporation rate set by \( P^* \), and this is only achieved in a vacuum, where \( P = 0 \).
Evaporation Rates - 2

- This can be viewed as two opposing fluxes:

\[
\frac{dN_e}{A_e dt} = \left(2\pi mk_B T\right)^{-1/2} \left(P^* - P\right)
\]

The net evaporation flux is the difference between the impingement rates for the two fluxes:
Evaporation Rates - 3

- Hertz only measured rates of about 1/10 of the above using Hg vapor.
- Knudsen postulated that the evaporant vapor molecules impinging upon the condensed phase surface may be reflected back.
  - $\alpha_v$ = sticking coefficient for vapor molecules onto the surface.
  - Then a $(1 - \alpha_v)$ fraction of the vapor molecules contribute to the evaporant pressure, but not to the evaporant flux.
  - Therefore, the vapor pressure must be higher by a factor of $1/\alpha_v$ to obtain the same evaporation rate.
- This gives the general Hertz-Knudsen equation:
  \[
  \frac{dN_e}{A_e \, dt} = \alpha_v \left(2\pi mk_B T\right)^{-1/2} \left(P^* - P\right)
  \]
Mass Evaporation Rates

• $\Gamma = \text{mass evaporation rate in g/cm}^2\text{-sec}$:

$$\Gamma = m \frac{dN_e}{A_e \, dt} = \alpha_v \left( \frac{m}{2\pi k_B T} \right)^{1/2} \left( P^* - P \right)$$

• For most elements, $\Gamma \sim 10^{-4} \text{ g/cm}^2\text{-sec}$ at $P^* = 10^{-2} \text{ torr}$.

• The mass of the evaporated material is

$$M_e = \int_0^t \int_0^{A_e} \Gamma \, dA_e \, dt$$
Free Evaporation Versus Effusion

• Evaporation from a free surface is termed Langmuir evaporation.

• Because $\alpha_v$ is often much less than unity, the general Hertz-Knudsen expression must be used.

• Effusion refers to evaporation through an orifice by which the area of the orifice appears as an evaporation source of the same area.

• Free evaporation is isotropic.

• Effusion is somewhat directional.
  – Ideally, it is a Lambertian angular distribution.
Equilibrium Vapor Pressure

• A working formulation of the equilibrium vapor pressure from standard thermochemical data is therefore:

\[
\ln P^* = -\frac{\Delta H_{eo} (298K)}{RT} + \frac{\Delta S_{eo} (298K)}{R} + \frac{1}{RT} \int_{298K}^{T} \int_{298K}^{T} \frac{\Delta c_p}{T} dTdT
\]

– \(P^*\) is in units of atmospheres.
– \(\Delta H_{eo}(298K), \Delta S_{eo}(298K), \text{and } c_p(T)\) may be found in standard tables of thermochemical data.
– Note: \(1 \text{kcal} = 1 \text{Cal} = 1000 \text{cal} = 4186.8 \text{J} = 3.97 \text{BTU}\)
– See Section D of the CRC Handbook of Chemistry and Physics.
– Example: Aluminum:
  • \(\Delta H_{eo}(298K) = 70 \text{kcal/mole}, \Delta S_{eo}(298K) = 30 \text{kcal/mole-K}, \text{at the boiling point of } P = 1 \text{ atm and } T = 2327^\circ\text{C} = 2600 \text{ K}.
  • \(\Delta H_{mo}(298K) = 2.57 \text{kcal/mole}, \text{at the melting point of } P = 1 \text{ atm and } T = 658.5^\circ\text{C} = 931.7 \text{ K}.

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Equilibrium Vapor Pressure

Temperature, K

Vapor Pressure, Torr

- Aluminum
- Gallium
- Indium
- Silicon
- Gold
- Platinum
- Chromium
- Titanium
Equilibrium Vapor Pressure

![Graph showing the equilibrium vapor pressure for different elements as a function of reciprocal temperature. The graph includes lines for Aluminum, Gallium, Indium, Silicon, Gold, Platinum, Chromium, and Titanium.](image-url)
Adsorption

• Adsorption is the sticking of a particle to a surface.

• Physisorption:
  – The impinging molecule loses kinetic (thermal) energy within some residence time, and the lower energy of the molecule does not allow it to overcome the threshold that is needed to escape.

• Chemisorption:
  – The impinging molecule loses its kinetic energy to a chemical reaction which forms a chemical bond between it and other substrate atoms.
Stages of Thin Film Growth

- Island Stage
- Coalescence Stage
- Channel Stage
- Continuous Film Stage
Modes of Thin Film Growth

(1) Volmer-Weber: (island growth):


(2) Frank-Van der Merwe: (layer growth; ideal epitaxy):


(3) Stranski-Krastanov: (layers + islands):

Electrochemical Deposition

• Introduction
• Electro-plating
• Immersion plating (electroless plating)
• References
Introduction

• Plating is basically an application of REDOX chemistry
  – Electro-plating
  – Electroless plating
• Large industry for finishing parts
• Use in microelectronics for bonding posts and recently for copper interconnects
• Heavily regulated by EPA (not a basement or garage operation)
REDOX: Reduction / Oxidation Reactions

- Electron transfer reactions

Oxidizing agent + n e⁻ = Reducing agent

Oxidation is a loss of electrons
Reduction is a gain of electrons

Oxidizing agents get reduced
Reducing agents get oxidized
Electroplating

- Copper object (cathode)
- Salt (nickel chloride) –molten or in water-
- Source of metal used for plating (anode)
- Nickel (ionic) gets REDUCED and gets deposited at the cathode
- Nickel (metal) gets OXIDIZED at the anode and gets into the solution
Electroplating @Home

- **Cathode**: is clean shiny US penny
- **Anode**: is sand down modern US penny (to expose zinc core)
- **Solution**: water based zinc salt
  - Vinegar
  - Add 100g/l Epsom salts
  - Add 120g/l table sugar
  - Mix in a pyrex container

Put zinc penny in the vinegar and let sit for a few hours (dissolve zinc).

Add epsom salts and table sugar.

Use a 1.5 Volt flashlight battery to supply the current.

Sit and watch your copper penny zinc plated (silvery coating).
Immersion plating (electroless plating)

With time, Cu plates out onto Zn metal strip, and Zn strip “disappears.”

- Zn is oxidized and is the reducing agent
  \[ \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \]

- Cu$^{2+}$ is reduced and is the oxidizing agent
  \[ \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s) \]
Green processes

• No cyanides
• No phosphates
• No caustic amines
• Commercial products employ proprietry chemistry that companies do not make public (such as our Technics plating solutions)
References

- [http://www.finishing.com](http://www.finishing.com) (general information)
- [http://www.finishing.com/Library](http://www.finishing.com/Library) (library)