MTLE-6120: Advanced Electronic Properties of Materials

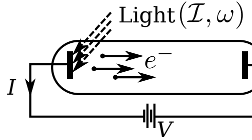
Metal-vacuum junctions: thermal and field emission

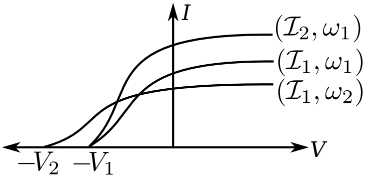
Reading:

- Kasap 4.9
- Review Kasap 3.1.2 (Photoelectric effect)

Photoelectric effect

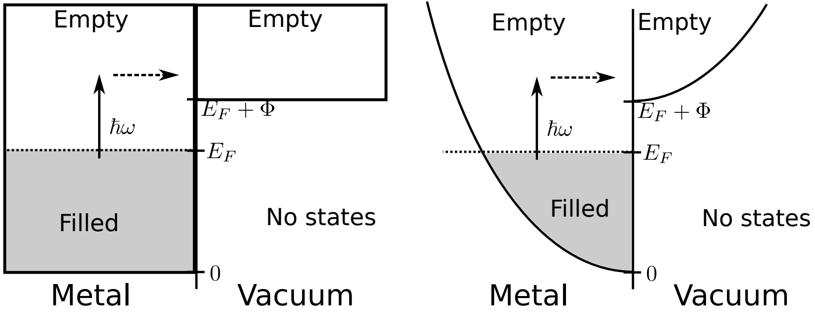
- Light ejects electrons from cathode $\Rightarrow I$ at $V = 0$
- $V \uparrow \Rightarrow I \uparrow$ till saturation (all ejected electrons collected)
- $V \downarrow \Rightarrow I \downarrow$ till $I = 0$:
  all electrons stopped at $V = -V_0$
- Increase intensity $\mathcal{I}$:
  higher saturation I but same stopping V
- Increase frequency ω:
  higher stopping V
- Stopping action: $eV_0 = \mathrm{KE}_{\mathrm{max}}$
- Experiment finds $eV_0 \propto (\omega - \omega_0)$
- In fact $eV_0 = \hbar(\omega - \omega_0)$
- Different cathodes $\Rightarrow$ different ω_0
  but same slope $\hbar$ identical to that
  from Planck's law!
- Light waves with angular frequency ω behave like
  particles (photons) with energy $\hbar\omega$ (Einstein, 1905)





Workfunction: energy level alignment with vacuum

- Minimum energy Φ required to free electron from material
- Photoelectric effect threshold is $\hbar\omega_0 = \Phi$
- Electrons emitted with kinetic energy $\mathrm{KE} = \hbar\omega - \hbar\omega_0$
- Determined by alignment of energy levels across metal-vacuum interface



What determines workfunction?

- Electron binding in bulk material (stongly bound $\Rightarrow$ higher Φ)
- Equally important: surface of the metal i.e. metal-vacuum interface
- Energy-level alignment sensitive to details of the surface
- Example: work functions (in eV) of single crystalline metal surfaces

Metal	(110)	(100)	(111)	Polycrystalline
Al	4.06	4.20	4.26	4.1 – 4.3
Au	5.12	5.00	5.30	5.1 – 5.4
Ag	4.52	4.64	4.74	4.3 – 4.7
Cu	4.48	4.59	4.94	4.5 – 5.1

- Values for polycrystalline metals averaged over facets (whose relative prominence depends on sample preparation)

Thermionic emission

- Overcome energy difference (barrier) using thermal energy
- Number of electrons above barrier:

$$\int_{E_F+\Phi}^{\infty} \mathrm{d}E g(E) f(E) \approx \int_{E_F+\Phi}^{\infty} \mathrm{d}E g(E) \exp \frac{-(E-E_F)}{k_B T}$$

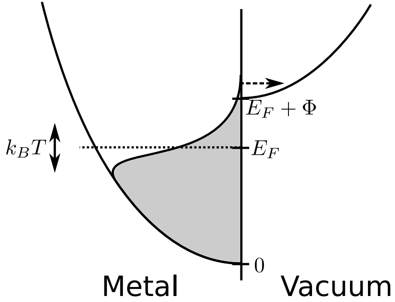
(assuming $\Phi \gg k_B T$, which holds for metals even at T_{melt})

- Can all these electrons cross?
- Need KE towards surface

$$\frac{m(v\cos\theta)^2}{2} > E_F + \Phi$$

- Current density per state:

$$\langle ev\cos\theta\rangle = \frac{ev(1-\frac{E_F+\Phi}{E})}{4}$$



Richardson-Dushman equation

- Current density of emitted electrons:

$$j = \int_{E_F+\Phi}^{\infty} \mathrm{d}E g(E) \exp \frac{-(E - E_F)}{k_B T} \cdot \frac{ev(1 - \frac{E_F+\Phi}{E})}{4}$$

- Assuming $\Phi \gg k_B T$ and free-electron $g(E) = 4\pi\sqrt{E}\left(\frac{\sqrt{2m}}{2\pi\hbar}\right)^3$:

$$j = \underbrace{\frac{4\pi e m k_B^2}{(2\pi\hbar)^3}}_{B_0} T^2 \exp \frac{-\Phi}{k_B T}$$

  with Richardson-Dushman constant $B_0 \approx 1.20 \times 10^6$ A/(mK)^2

- Additional consideration: electrons with sufficient KE can still be reflected
- Include energy-dependent reflection coefficient in above consideration
- Modified $B_e \lesssim B_0/2$ for most metals, $\ll B_0$ for some d-metals (why?)

Electron near a metal surface

- Metal surface at constant potential; electric field normal
- Electric field outside as if due to charge and its reflection

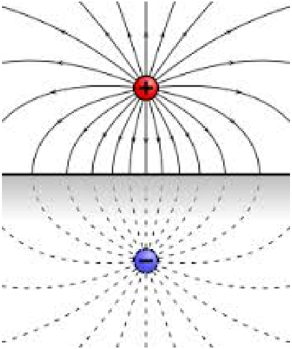
$$E(\vec{r}) = \frac{q(\vec{r} - z\hat{z})}{4\pi\epsilon_0|\vec{r} - z\hat{z}|^3} - \frac{q(\vec{r} + z\hat{z})}{4\pi\epsilon_0|\vec{r} + z\hat{z}|^3}$$

- Force on charge:

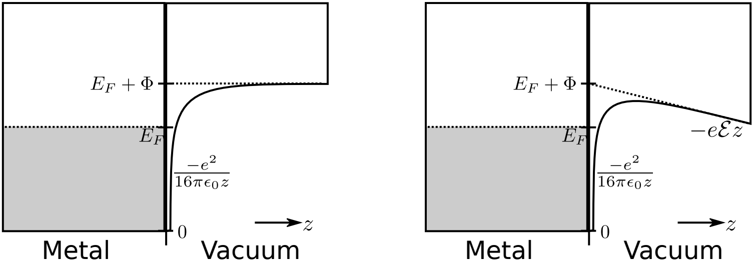
$$\vec{F} = \frac{-q^2\hat{z}}{4\pi\epsilon_0(2z)^2}$$

- Potential energy:

$$U = -\int_{\infty}^{z} \vec{F} \cdot \hat{z} = \frac{-q^2}{16\pi\epsilon_0 z}$$



Schottky effect



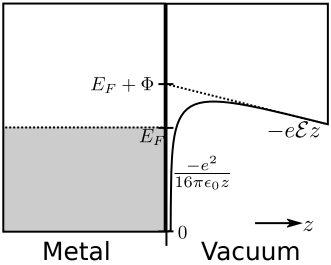
- Image charge effect changes energy level diagram (horizontal axis is now distance from interface)
- What is the energy barrier for electrons at E_F?
- Now consider an applied electric field $\mathcal{E}$
- Net minimum energy level of electron is now:

$$E_{\min}(z > 0) = E_F + \Phi - \frac{e^2}{16\pi\epsilon_0 z} - e\mathcal{E}z \quad \leq \quad E_F + \Phi - \sqrt{\frac{e^3\mathcal{E}}{16\pi\epsilon_0}}$$

- Barrier reduced to $\Phi - \beta_s\sqrt{\mathcal{E}}$ with Schottky coefficient $\beta_s = \sqrt{e^3/(16\pi\epsilon_0)} \approx 3.79 \times 10^{-5}$ eV/$\sqrt{\text{V/m}}$

Field emission

- Electric field reduces effective barrier for electron emission
- Still use thermal energy, but with a lower barrier $\Rightarrow$ use lower T
- Technically field-assisted thermionic emission
- Use sharpened metal tips / nanowires / nanotubes to enahance local $\mathcal{E}$
- So far, considered electrons thermally excited across barrier
- Will there be a current at $T = 0$?



Fowler-Nordheim tunneling

- Consider very strong electric field $\mathcal{E}$; neglect Schottky effect
- Minimum energy of electron in vacuum $E_{\min}(z) \approx E_F + \Phi - e\mathcal{E}z$
- Electrons in metal with energy $E < E_F$ have less than minimum energy for $0 < z < \frac{E_F + \Phi - E}{e\mathcal{E}}$
- Tunneling probability, accounting for z-KE:

$$T(p_z) \approx \exp \frac{-2\int \mathrm{d}z \sqrt{2mE_{\min}(z) - p_z^2}}{\hbar} \approx \exp \frac{-4\sqrt{2m}\left(E_F + \Phi - \frac{p_z^2}{2m}\right)^{3/2}}{3e\hbar\mathcal{E}}$$

  (based on the semi-classical WKB approximation for wavefunctions)
- Tunneling current:

$$j = \int_{p<p_F} \frac{\mathrm{d}\vec{p}}{(2\pi\hbar)^3} \frac{ep_z}{m} T(p_z) \approx \frac{e^3}{16\pi^2\hbar\Phi}\mathcal{E}^2 \exp \frac{4\sqrt{2m\phi^3}}{3e\hbar\mathcal{E}}$$

- Identical dependence with $\mathcal{E}$, as thermionic emission had with T (even though one strictly classical, other quantum mechanical)