

Lecture 7

Work Function; Electron Emission

Outline:

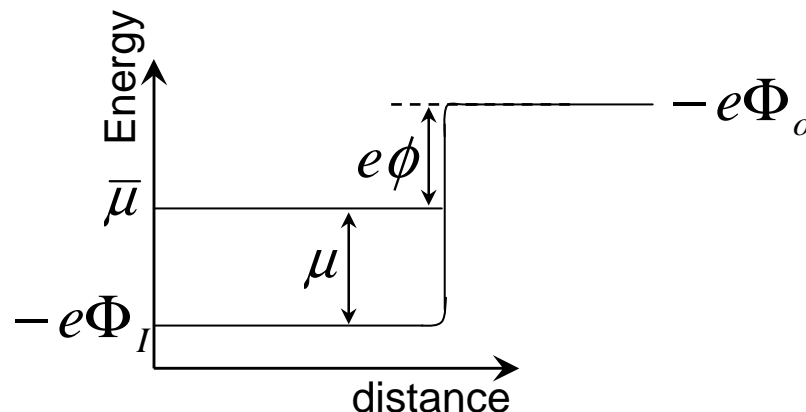
1. Work Function
2. Electron Emission
 - A. Thermionic Emission
 - B. Field Emission
 - C. Secondary Electron Emission
3. Measurements of Work Function

References:

- 1) Zangwill, p.57-63
- 2) Woodruff & Delchar, pp. 410-422, 461-484
- 3) Luth, pp.336, 437-443, 464-471
- 4) A. Modinos, "Field, Thermionic and Secondary Electron Spectroscopy", Plenum, NY 1984.

7.1 Work Function: Uniform Surfaces

- The “true work function” $e\phi$ of a uniform surface of an electronic conductor is defined as the difference between the electrochemical potential $\bar{\mu}$ of the electrons just inside the conductor, and the electrostatic potential energy $(-e\Phi_o)$ of an electron in the vacuum just outside
- $\bar{\mu}$ is work required to bring an electron isothermally from infinity to solid



$$\bar{\mu} = \left(\frac{\partial G}{\partial n_e} \right)_{T,P} \quad (5.1)$$

$$e\phi = -e\Phi_o - \bar{\mu} \quad (5.2)$$

$$\phi = -\Phi_o - \frac{\bar{\mu}}{e} \quad (5.3)$$

- Note: $\bar{\mu}$ is function of internal AND surface/external (e.g., shifting charges, dipoles) conditions;
- We can define quantity μ which is function of internal state of the solid

Chemical potential of electrons: $\mu = \bar{\mu} + e\Phi_i$ ← Average electrostatic potential inside

Work Function

- The Fermi energy [E_F], the highest filled orbital in a conductor at $T=0K$, is measured with respect to $(-e\Phi_I)$ and is equivalent to μ .
- We can write:
$$e\phi = -e\Phi_o + e\Phi_I - \mu \quad (5.4)$$
$$\phi = \Delta\Phi - \frac{\mu}{e} \quad (5.5)$$
- $\Delta\Phi$ depends on surface structure and adsorbed layers. The variation in ϕ for a solid is contained in $\Delta\Phi$.
- What do we mean by potential just outside the surface???

Potential just outside the surface

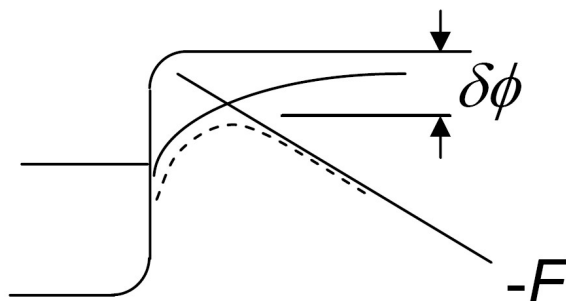
The potential experienced by an electron just outside a conductor is:

$$V(r) = -\frac{k_e e}{4r} = -\frac{e}{16\pi\epsilon_0} = 8.99 \times 10^9 \frac{Nm^2}{C} \quad (5.6)$$

For a uniform surface this corresponds to Φ_0 in (5.1):

$$V(r) \rightarrow 0 \text{ as } r \rightarrow \infty \text{ [in mV range for } r \geq 10^3 \text{ \AA}]$$

In many applications, an accelerating field, F , is applied:



$$V(r) = -Fr - \frac{k_e e}{4r} \quad (5.7)$$

$$\left. \frac{dV}{dr} \right|_{r=r_0} = 0$$

$$r_0 = \left(k_e \frac{e}{4} \right)^{1/2} \frac{1}{F^{1/2}} = \frac{1.9 \times 10^{-5}}{F^{1/2}} m \quad (5.8)$$

$$\delta\phi = (k_e e F)^{1/2} = 3.79 \times 10^{-5} F^{1/2} \text{ Volts (} F \text{ in Volts/m)} \quad (5.9)$$

$$\text{For } F = 10^4 \text{ Volts/m (100 V/cm), } r_0 = 1.9 \times 10^{-7} m = 1900 \text{ \AA} \quad \delta\phi = 3.8 mV$$

$$\delta\phi \propto F^{1/2}$$

Selected Values of Electron Workfunctions*

Element	ϕ (eV)	Element	ϕ (eV)	Element	ϕ (eV)
Ag	4.26	Cu	4.65	Si	4.85
Ag (100)	4.64	Cu(100)	4.59	Ru	4.71
Ag (110)	4.52	Cu(110)	4.48	Ta	4.25
Ag (111)	4.74	Cu(111)	4.98	Ta (100)	4.15
Ba	2.52	Ir (110)	5.42	Ta (110)	4.80
C	5.0	Ir(111)	5.76	Ta (111)	4.00
Ce	2.9	K	2.30	Ti	4.53
Cr	4.5	LaB ₆	2.66	W	4.55
Cs	2.14	Mo	4.60	Zr	4.05

Units: eV electron Volts;

*Reference: CRC handbook on Chemistry and Physics version 2008, p. 12-114.

Work Function: Polycrystalline Surfaces

Consider polycrystalline surface with “patches” of different workfunction, and different value of surface potential

i, Φ_{oi}	j, ...	k	l
m	m	o	p

At small distance r_o above i^{th} patch electrostatic potential is Φ_{oi}

At distances large w/r/t/ patch dimension:

$$\Phi_o = \sum_i f_i \Phi_{oi}, f_i = \text{fractional area of } i^{\text{th}} \text{ patch}$$

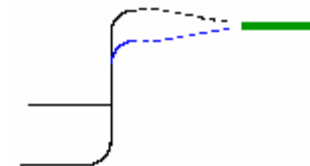
So mean work function is given by:

$$e\bar{\phi} = \sum_i f_i e\phi_i \quad (5.10)$$

- at **low** applied field, electron emission controlled by: $e\bar{\phi}$

- at **high** field (applied field \gg patch field)

electron emission related to individual patches: $e\phi_i$



On real surfaces, patch dimension $< 100\text{\AA}$, if $\Delta\phi \sim 2 \text{ eV}$ then patch field $F \sim 2V/(10^{-6} \text{ cm}) \sim 2 \times 10^6 \text{ Volts/cm}$. work required to bring an electron from infinity to solid

Workfunction

Factors that influence work function differences on clean surfaces:

- Adsorbed layers
- Surface dipoles (cf. Zangwill, p 57)
- Smooth surface: electron density “spillover”

- Electron density outside rough surface
- For tungsten

$e\phi$, eV	W plane
5.70	(110)
4.93	(211)
4.39	(111)
4.30	(116)

Fig. 4.2. Electron density profile at a jellium surface for two choices the background density, r_s (Lang & Kohn, 1970).

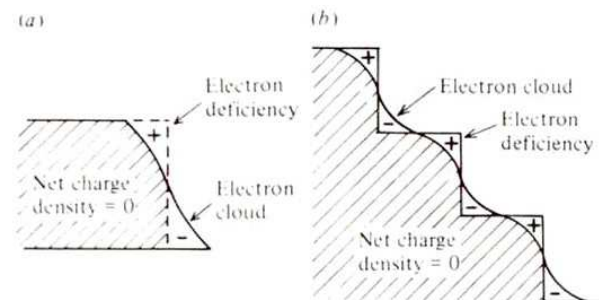
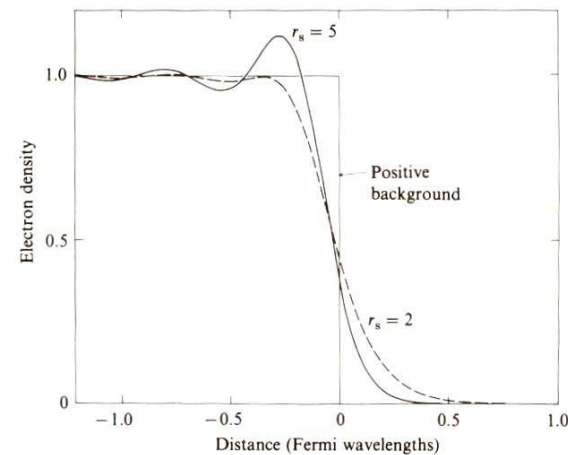
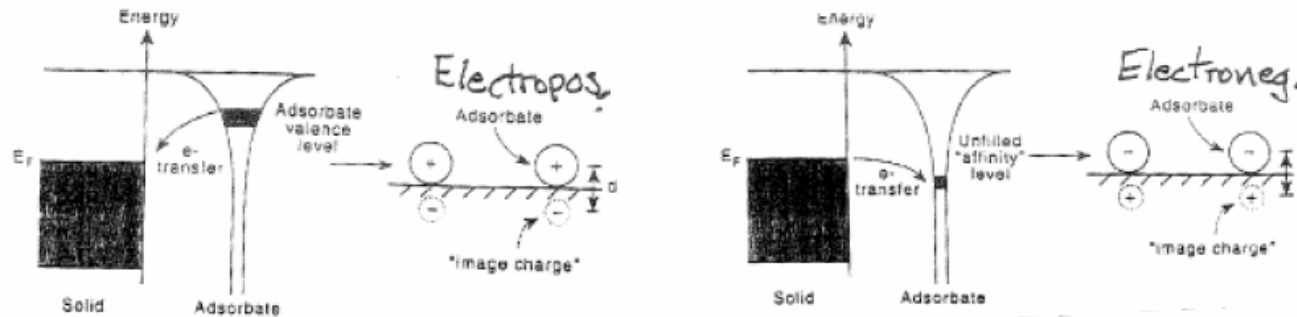


Fig. 7.2 Charge distribution at a metal surface (schematic): (a) an atomically smooth surface; (b) an atomically stepped surface.

Work function change upon adsorption

- Charge transfer at interface: electro**positive** (K, Na, ...) or electro**negative** (Cl, O, F, ...)

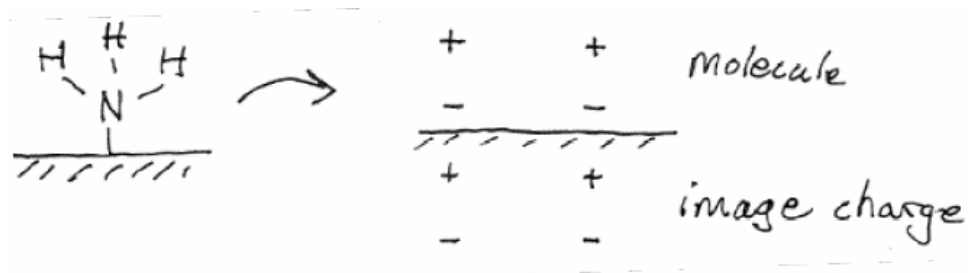


- Model dipole layer as parallel plate capacitor:

$$\Delta\phi = \frac{n\mu}{\epsilon_0} \quad \mu - \text{dipole moment [C m]}; n - \text{surface charge density [m}^{-2}\text{]}; \epsilon_0 = 8.85 \times 10^{-12} [\text{C / Vm}]$$

Suppose $\Delta\phi = 1.5\text{V}$ for $1 \times 10^{15}/\text{cm}^2$ O atoms on W (100). What is μ ?

For molecules with a permanent dipole moment:



7.2.1 Electron Sources: Thermionic Emission

Thermionic emission occurs when sufficient heat is supplied to the emitter so that e's can overcome the work function, the energy barrier of the filament, E_w , and escape from it

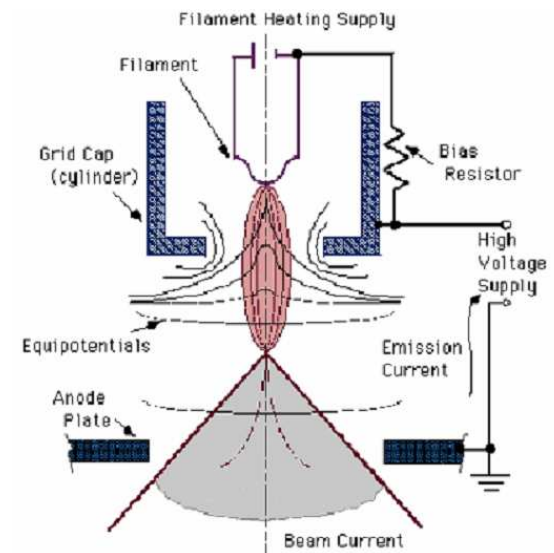
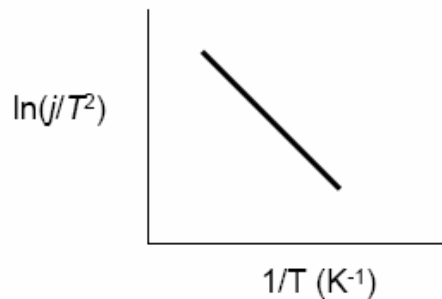
- **Richardson's Equation:** (derivation – aside)

$$\text{Current density, } j: \quad j = A_o(1 - \bar{r})T^2 \exp\left(-\frac{e\phi}{kT}\right)$$

$$r = \text{reflection coefficient; } A_o = \frac{4\pi me k^2}{h^3} = 120.4 \frac{\text{Amp}}{\text{cm}^2 \text{ deg}^2}$$

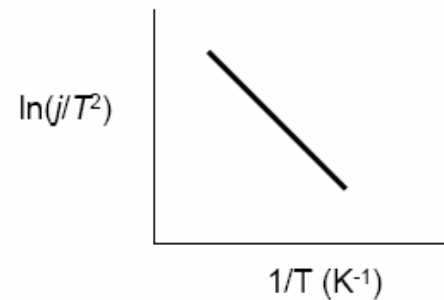
- **Richardson plot:**

$\ln(j/T^2)$ vs $1/T \Rightarrow$
 \Rightarrow straight line



7.2.1 Electron Emission: Thermionic Emission

- **Richardson plot:**
 $\ln(j/T^2)$ vs $1/T \Rightarrow$
 \Rightarrow straight line



- **Schottky Plot**

$$e\phi \rightarrow e\Phi_o - bF^{1/2} \quad (\text{cf. eq.5.9})$$

$$\ln j \text{ vs } F^{1/2} \Rightarrow \text{straight line}$$

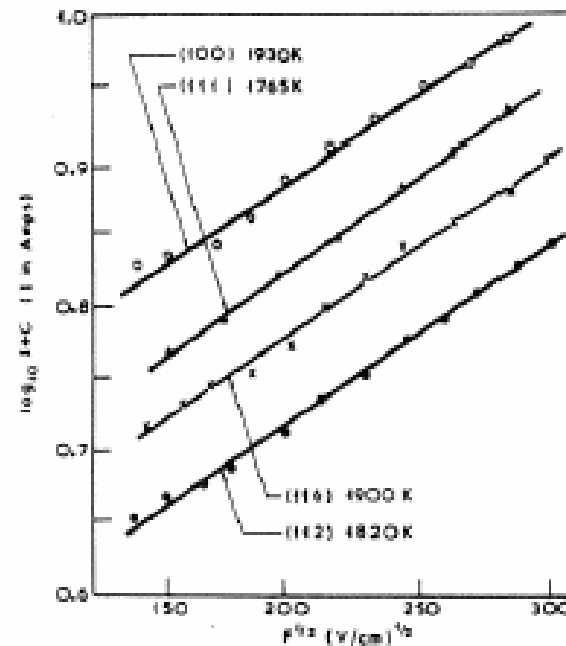


FIGURE 2-3

Schottky plots for four faces of tungsten. $C = 8, 9, 7.9, 8.0$ for the (100), (111), (110), and (112) planes, respectively. (From Smith, 1954).

7.2.2 Field Electron Emission

- Electron tunneling through low, thin barrier
 - Field emission, when $F > 3 \times 10^7$ V/cm ~ 0.3 V/Å
- General relation for electron emission in high field:

$$j = e \int_0^{\infty} P(E_Z, F) v(E_Z) dE_Z$$

- P is given by WKB approximation

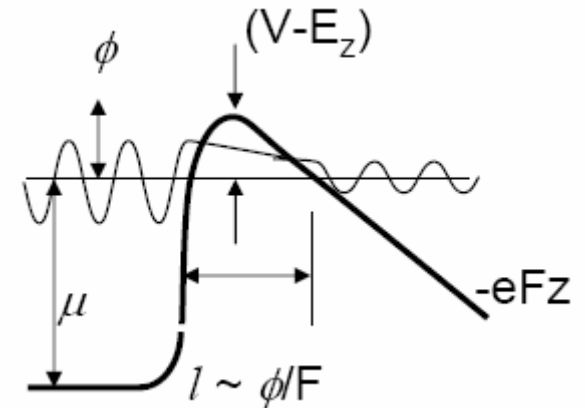
$$P = \text{const} \times \exp\left(-\frac{2^{2/3} m^{1/2}}{\hbar} \int_0^l (V - E_Z)^{1/2} dz\right)$$

- If approximate barrier by triangle: $\int \sim \frac{1}{2} \phi^{1/2} \frac{\phi}{F} \sim \frac{1}{2} \frac{\phi^{3/2}}{F}$

$$P = \text{const} \times \exp\left(-\frac{2^{2/3} m^{1/2}}{\hbar} \frac{\phi^{3/2}}{F}\right)$$

- Fowler – Nordheim eqn, including potential barrier:

$$j = 1.54 \times 10^{-6} \frac{F^2}{\phi} t^2(y) \exp\left\{-6.83 \times 10^7 \frac{\phi^{3/2} f(y)}{F}\right\}; \text{ where } y = \frac{e^{3/2} F^{1/2}}{\phi}$$



How do we get high fields: Field Emission Microscope!

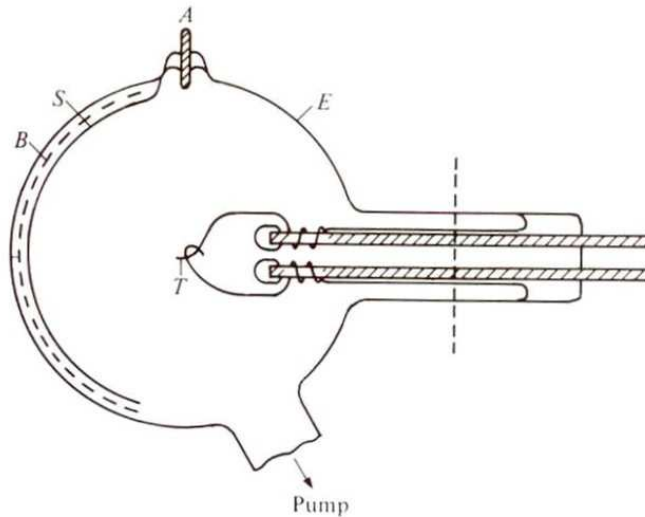


Fig. 6.5 Schematic drawing of one form of the field emission microscope. *E*, glass envelope; *S*, phosphorescent screen; *B*, tin oxide backing; *A*, anode connector; *T*, emitter tip.

Get high field by placing sharp tip at center of spherical tube.

Mag: $R/r \sim 5\text{cm}/10^{-5}\text{cm} \sim 500,000$

$F = cV$; $c \sim 5/r$ $F \sim 5 \times 10^7 \text{ V/cm}$

For $V = 2,500 \text{ Volts}$.

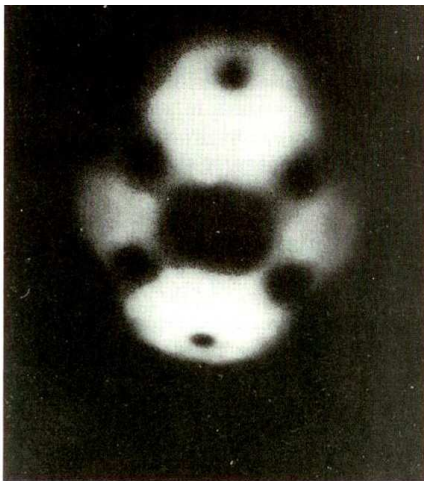


Fig. 6.7 Field emission image from a clean W field emitter showing the symmetry typical of such patterns.

W single crystal wire as tip.
Typical pattern on phosphor screen

Field Emission Properties

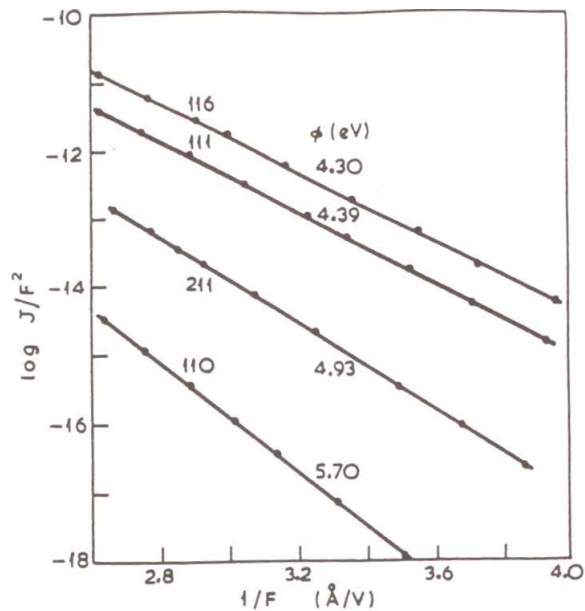
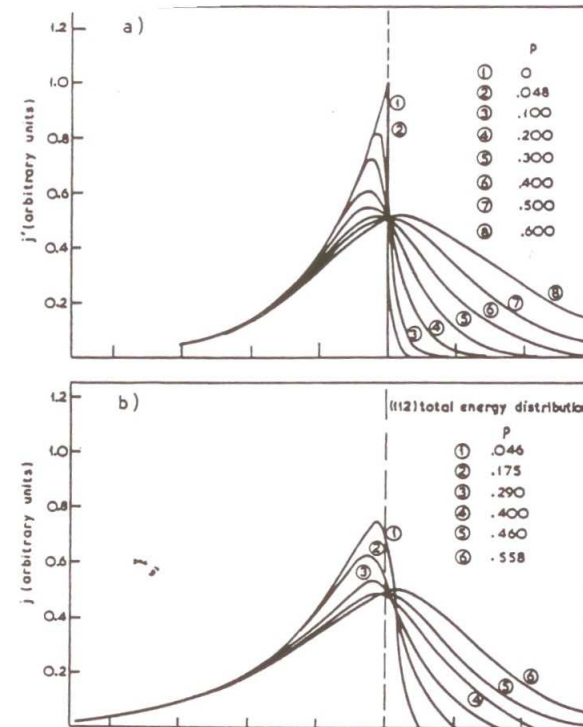


FIGURE 1.5

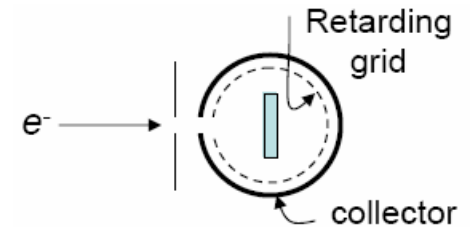
Fowler-Nordheim plots of field emission from the (116), (111), (211), and (110) planes of tungsten (From Müller, 1955.)



(a) Theoretical total energy distributions [Eq. (1.88)] at various values of p . (b) Experimental total energy distributions from the (112) plane of tungsten at various values of p , where $d_0 = 0.146$ eV and $F = 3.48 \times 10^7$ V/cm.

7.2.3 Secondary Electron Emission

Electrons emitted from surfaces after electron bombardment
 In general complicated phenomenon
 involving several interrelated processes



Generally classify secondaries into three categories:

- (I) Elastic ;
- (II) Inelastic;
- (III) “true” secondaries (KE < 50 eV)

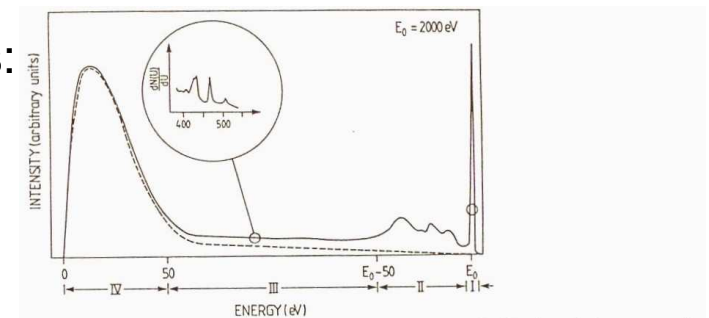


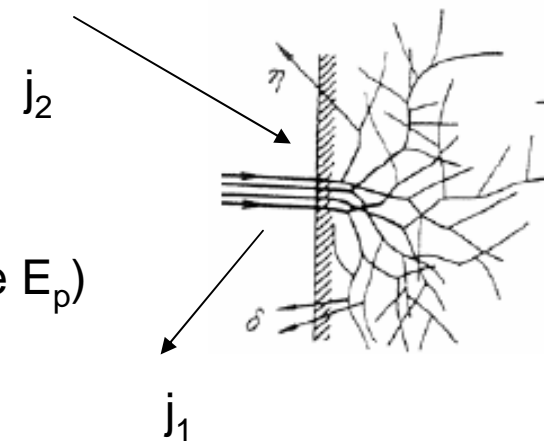
Fig. V.2. Qualitative large-scale overview of the energy distribution of electrons emitted from a surface which is irradiated by an electron beam of primary energy E_0 .

Total coefficient for secondary emission,

$$\sigma = j_2/j_1 = r + \eta + \delta$$

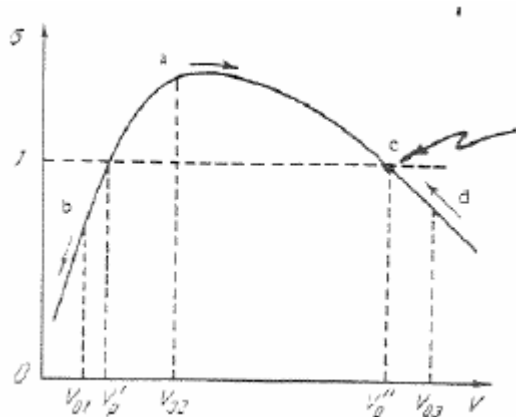


For metals, max values: $r \sim 0.2$ ($E_p \sim \text{eV}$); $\eta \sim 0.02$ (large E_p)
 $\eta \sim 0.3$ to 0.4 ; $\delta \sim 0.5$ to 1.8 ($E_p \sim \text{few hundred eV}$)
 For insulators, σ can be MUCH higher (~ 20 !!!!)



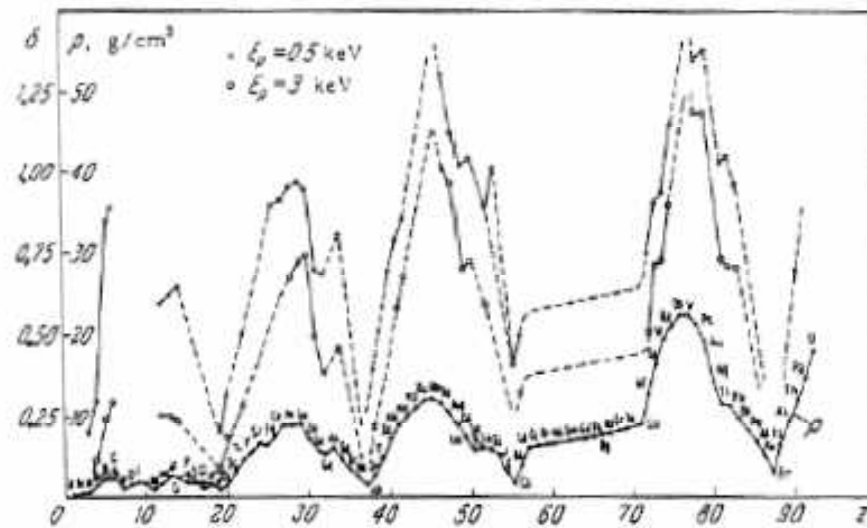
Secondary Electron Emission

- Establishment of stable potential for insulators and dielectric materials



In practice, steady state potential reached by dielectric is due mainly to incomplete extraction of secondary electrons

- For metals and semiconductors: Correlation between δ and density, ρ



7.3 Measurements of Workfunction

Absolute value of ϕ

A. Photoemission

$$\phi = h\nu - W$$

W = full width of energy distribution

B. Thermionic Emission (Richardson's Equation)

C. Field Emission Retarding Potential (FERP)

Workfunction difference

A. Shelton Method

B. Vibrating Capacitor – Kelvin Probe

<http://www.kelvinprobe.info/>