Surface and Interface Science
Physics 627; Chemistry 541

Lecture 11
Oct. 7 2010

Intro to Electronic Properties:
Work Function, Thermionic Electron Emission, Field Emission

References:

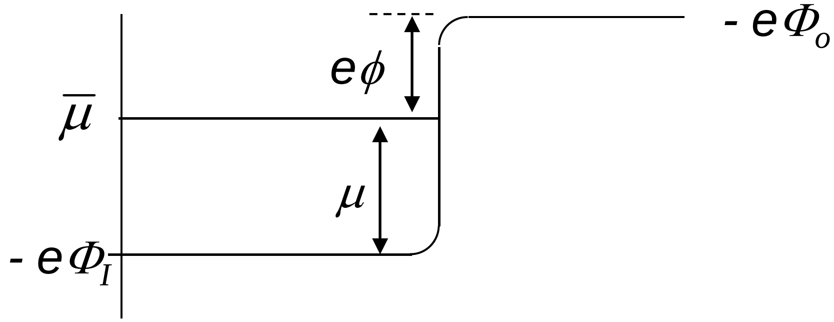
1) Woodruff & Delchar, Pp. 410-422; 461-484
2) Zangwill Pp. 57 – 63
3) C. Herring and M.N. Nicholas, "Thermionic Emission" Rev. Mod. Phys **21**, 185 (1949)
4) A. Modinos, "Field, Thermionic, and Secondary Electron Spectroscopy (Plenum, NY, 1984)
5) L.N. Dobretsov and M.V. Gomoyunova "Emission Electronics" (Keter Press, Jerusalem, 1971)

Work Function

Uniform Surface

- True work function, $e\phi$, of conductor is difference between electrochemical potential, $\bar{\mu}$, of electron just inside 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 from infinity to solid



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

$$e\phi = -e\Phi_o - \bar{\mu}$$

$$\phi = -\Phi_o - \bar{\mu} / e$$

Note: $\bar{\mu}$ is function of internal AND surface/external (e.g., shifting charges, dipoles) conditions. 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 = 0 K, is measured with respect to $-e\Phi_I$ and is equivalent to μ.

•We can write: $e\phi = -e\Phi_o + e\Phi_I - \mu$ or equivalently: $\phi = \Delta\Phi - \mu / e$

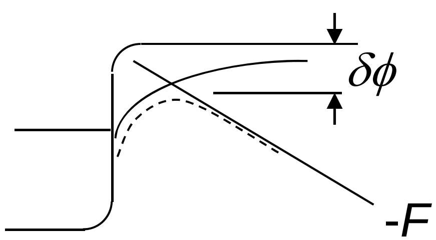
- $\Delta\Phi$ depends on surface structure and adsorbed layers. The variation in ϕ for a solid is contained in $\Delta\Phi$.

What do we mean by potential just outside the surface???

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

$$V(r) = -\frac{k_e e}{4r} \quad \text{where} \quad k_e = \frac{1}{4\pi\varepsilon_o} = 8.99\times 10^9 \ \text{Nm}^2/\text{C}$$

.For a uniform surface, this corresponds to Φ_o in (1) (V(r) → 0 as r → ∞ [in mV range for r > 10^3 Ang.])



In presence of electric field *-F*

$$V(r) = -Fr - \frac{k_e e}{4r} \qquad \left.\frac{dV}{dr}\right|_{r=r_o} = 0 \qquad r_o = \left(\frac{k_e e}{4}\right)^{1/2} \frac{1}{F^{1/2}} = \frac{1.9\times 10^{-5}}{F^{1/2}}$$

$$\delta\phi = \left(k_e e F\right)^{1/2} = 3.79\times 10^{-5} F^{1/2}$$

So for F = 10^4 V/m (100V/cm), r_o = 1.9 x 10^{-7} m; $\delta\phi$ = 3.8 mV

Work Function

Polycrystalline Surface

- patches of different work function → patches of different surface potential

- For small distance r_o above ith patch electrostatic potential is Φ_{oi}

i	j	k	…

At distances large w/r/t patch dimension:

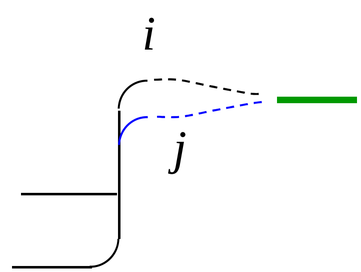
$$\Phi_o = \sum_i f_i \Phi_{oi}$$

So mean work function is given by:

$$e\overline{\phi} = \sum_i f_i e\phi_i$$

At low field, electron emission controlled by: $e\overline{\phi}$

At high field (applied field >> patch field) electron emission related to individual patches $e\phi_i$.



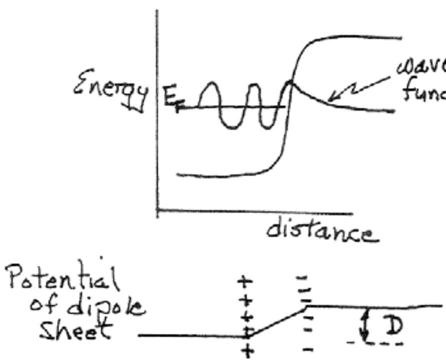
On real surfaces, patch dimension <~ 100Ang, if $\Delta\phi$ ~ 2 eV then patch field F ~ 2V/10^{-6} cm ~ 2 x 10^6 V/cm. Work required to bring an electron from infinity to solid

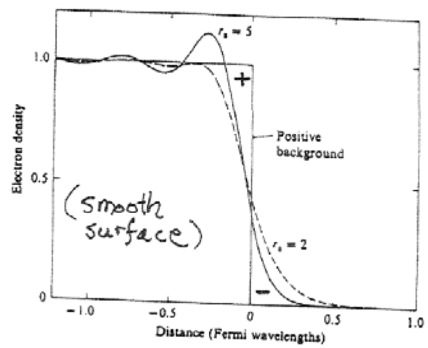
Work Function

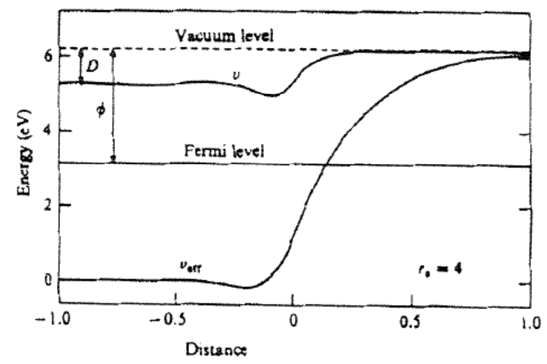
Factors that influence work function differences on clean surfaces

- adsorbed layers
- surface dipole

•SMOOTH SURFACE: Electron density "spillover"



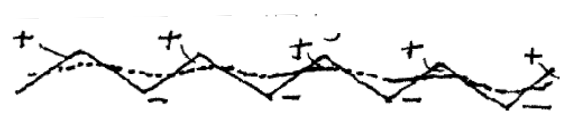




- OUTSIDE ROUGH SURFACE: "Smoothing" contribution <u>lowers</u> ϕ

•Example:

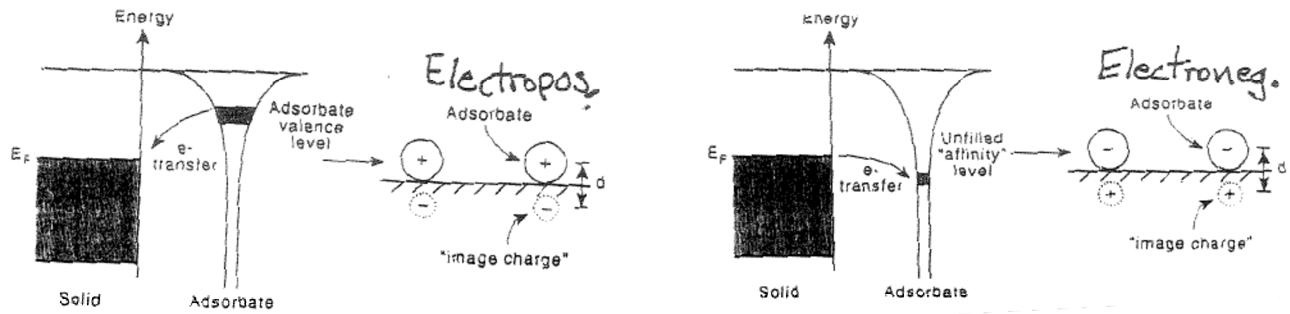
W	$e\phi$
(110)	5.70
(211)	4.93
(111)	4.39
(116)	4.30



Work Function

Work function change upon adsorption

- Charge transfer at interface: electropositive (K, Na, …)
  Electronegative (Cl, O, F, …)



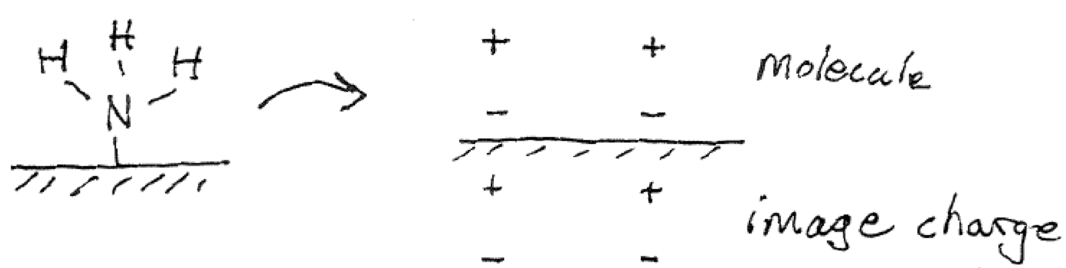
•Model dipole layer as parallel plate capacitor:

- $\Delta\phi = n\mu/\varepsilon_o$

μ = diople moment (C.m)
n = surface density (m^{-2})
ε_o = 8.85 X 10^{-12} C/Vm

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

For molecules with permanent dipole moments:



Electron Emission

Thermionic emission

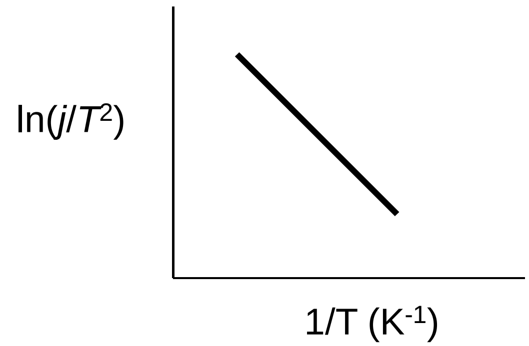
- RICHARDSON'S EQUATION

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

  $\bar{r}$ = reflection coefficient $$A_o = \frac{4\pi mek^2}{h^3} = 120.4 \frac{Amp}{cm^2 \deg^2}$$

- Richardson plot:

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



- Schottky Plot

  $e\phi \rightarrow e\phi - bF^{1/2}$

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

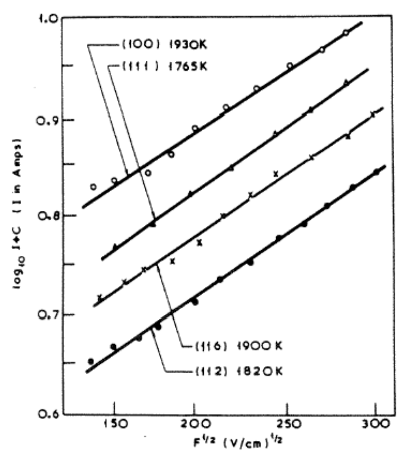


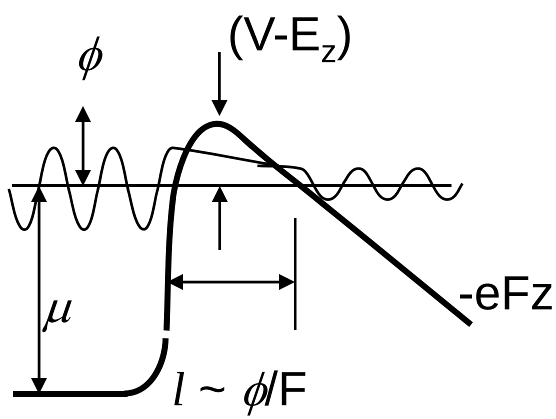
FIGURE 2.3

Schottky plots for four faces of tungsten. C = 8, 9, 7.9, 8.0 for the (100), (111), (116), and (112) planes, respectively. (From Smith, 1954).

Electron Emission

Field emission

- Electron tunneling through low, thin barrier
  Field emission when F >~ 3 x 10^7 V/cm
  ~ 0.3 V/Ang



- General relation for electron emission in high field:

$$j = e\int_0^\infty P(E_z, F)v(E_z)dE_z$$

- P given by WKB approximation

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

- Approximate barrier by triangle → $\int = A \sim \frac{1}{2}\phi^{1/2}\frac{\phi}{F} \sim \frac{1}{2}\frac{\phi^{3/2}}{F}$

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

Fowler-Nordheim Eqn, including potential barrier:

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

where $y = \frac{e^{3/2}F^{1/2}}{\phi}$

t(y), f(y) slowly varying elliptic functions

Alternatively: $\frac{I}{V^2} = a\exp\left\{-\frac{b\phi^{3/2}}{cV}\right\}$ with F = cV

Electron Emission

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.

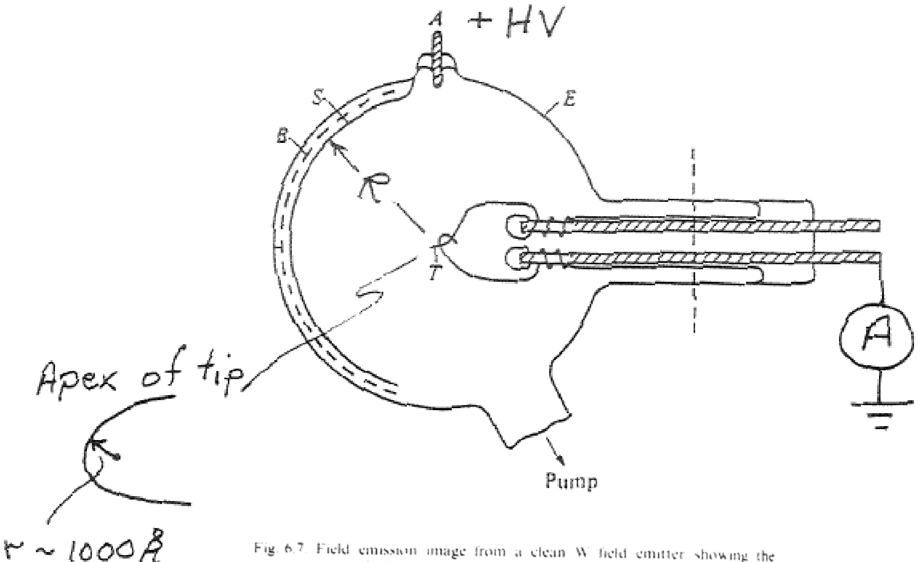
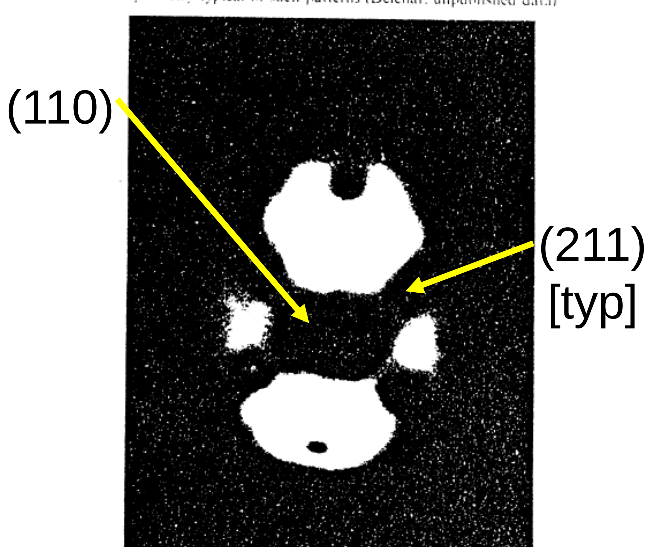


Fig. 6.7 Field emission image from a clean W field emitter showing the symmetry typical of such patterns (Delchar, unpublished data)



Field Emission Microscope

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

Mag: R/r ~ 5cm/10^{-5}cm ~ 500,000

F = cV; c ~ 5/r → *F* ~ 5 x 10^7 V/cm
For V = 2,500 Volts.

W single crystal wire as tip.

Typical pattern on phosphor screen

Electron Emission

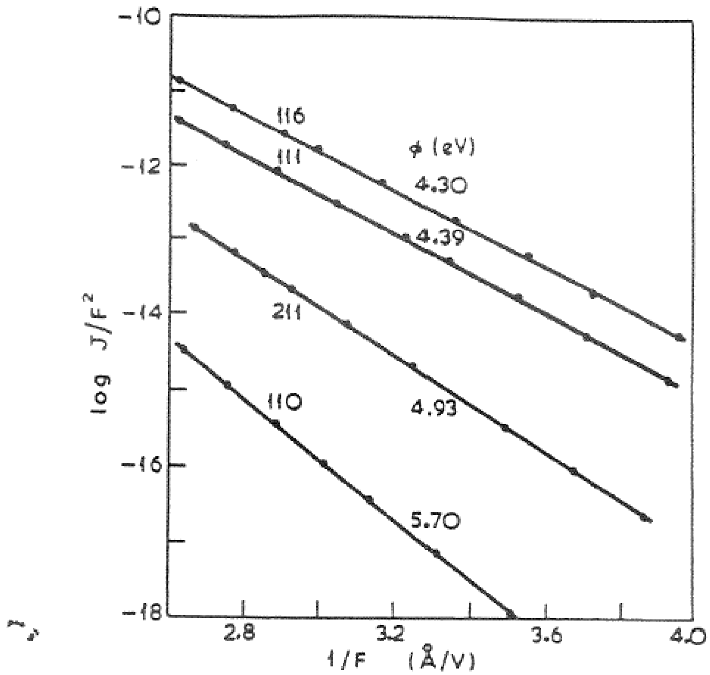
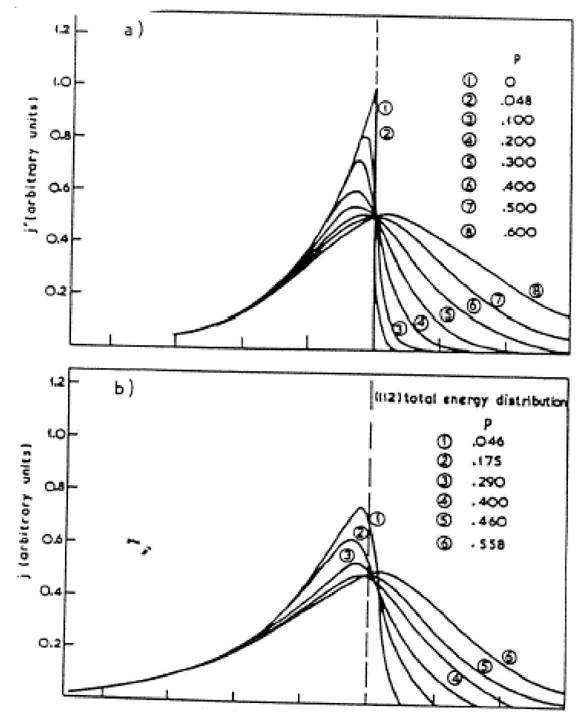


FIGURE 1.5

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

Field Emission Microscope

Field emission properties

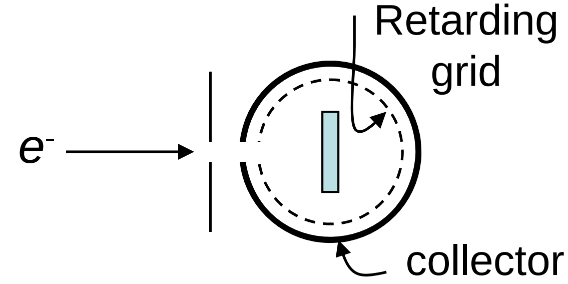


(a) Theoretical total energy distributions [Eq. (1.88)] at various values of p. (b) Experimental total energy distributions from the (112) plane of tungsten at various values of p, where $d_0 = 0.146$ eV and $F = 3.48 \times 10^7$ V/cm.

Electron Emission

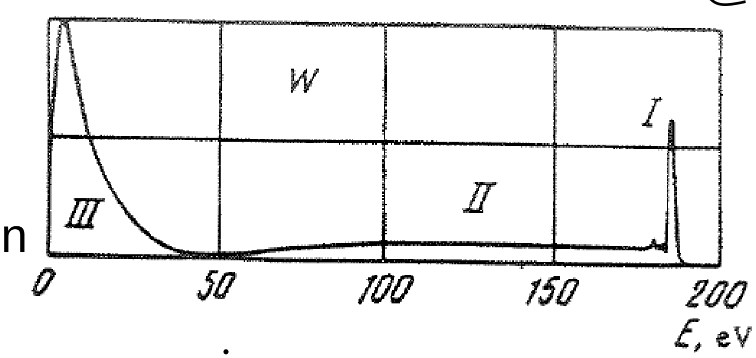
Secondary Electron Emission

Electrons emitted from surfaces after electron bombardment



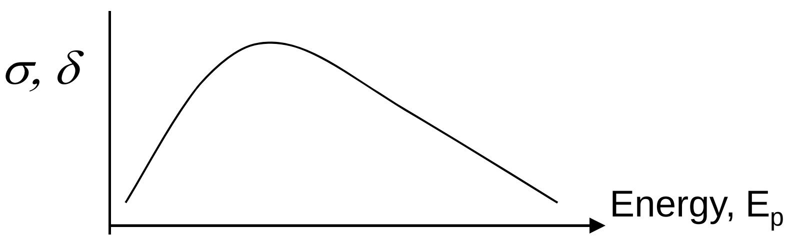
In general complicated phenomenon
involving several interrelated processes

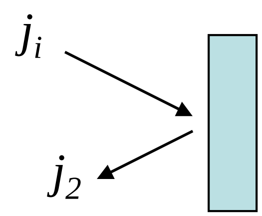
Generally classify secondaries into
three categories:
(I) Elastic ; (II) Inelastic;
(III) “true” secondaries (KE < 50 eV)

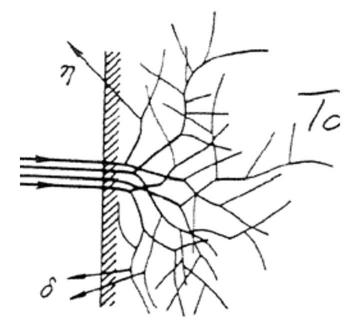


Total coefficient for secondary emission

$$\sigma = j_2/j_i = \overset{\text{I}}{r} + \overset{\text{II}}{\eta} + \overset{\text{III}}{\delta}$$







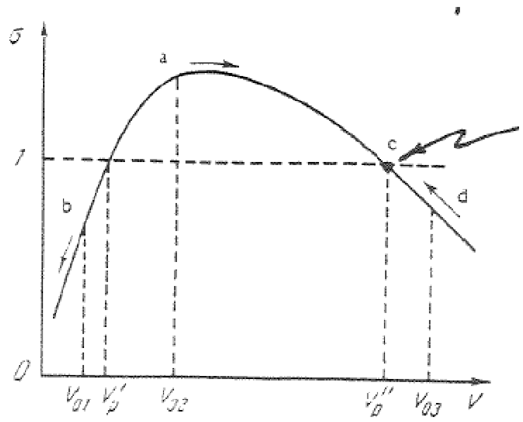
For metals, max values: r ~ 0.2 (E_p ~ eV); ~ 0.02 (large E_p)
η ~ 0.3 to 0.4
δ ~ 0.5 to 1.8 (E_p ~ few hundred eV)

For insulators, σ can be MUCH higher (~ 20!!!!)

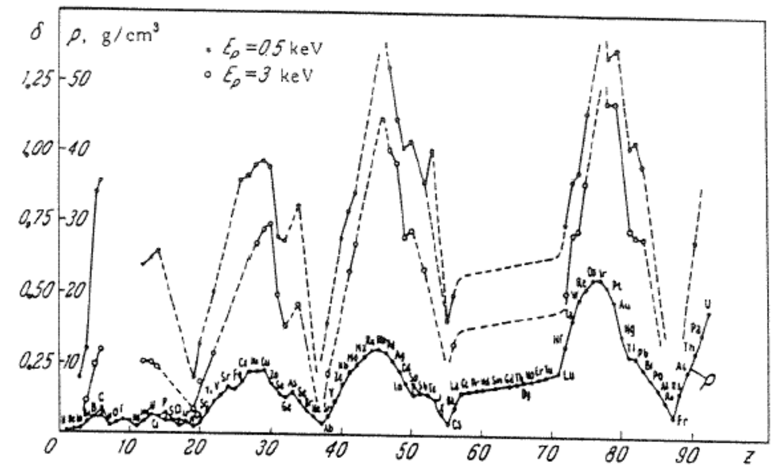
Electron Emission

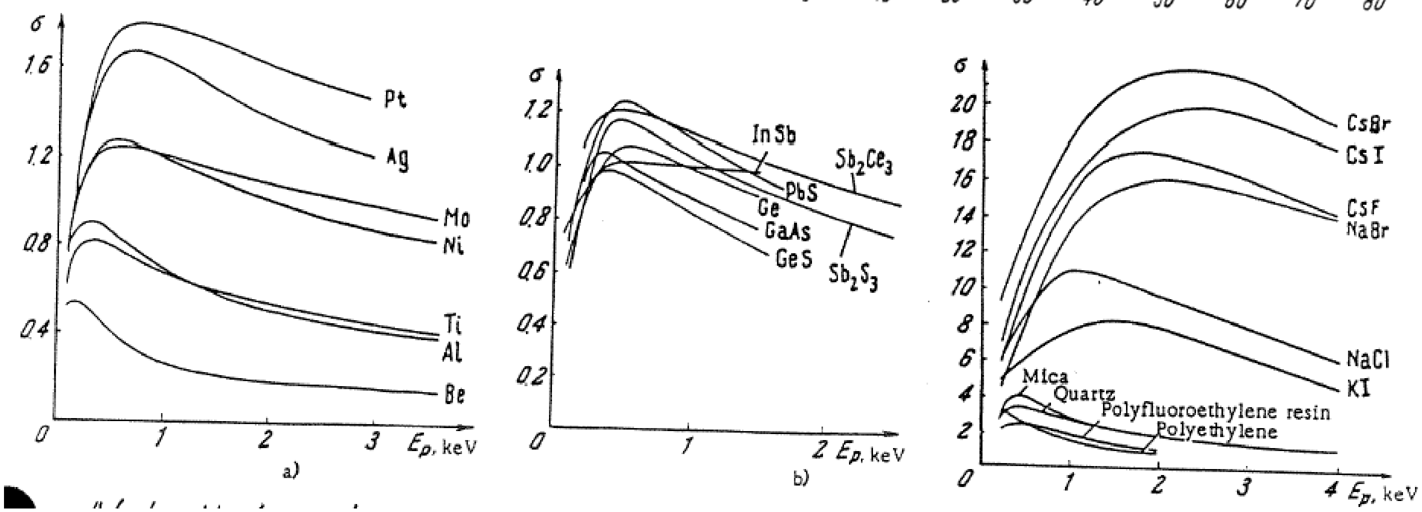
Secondary Electron Emission

Establishment of
stable potential for insulators



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





(NOTE: σ depends on work function, temp, angle of incidence, ….)