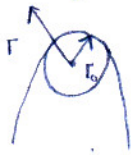
Finally, we briefly discuss two microscopic methods making use of work function contrast, or: visualizing work function.

(i) FEM = field emission microscope

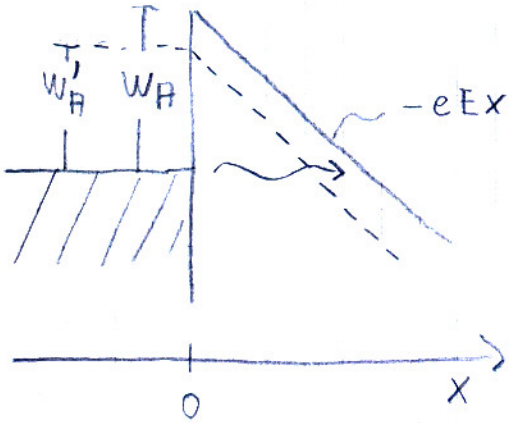
As shown in Fig. 3.14, electrons are extracted from a sharp tip by putting it at a high negative voltage with respect to a phosphor screen. Emitted electrons are accelerated radially onto the screen, where they give a work function image of the tip.

At the surface of a sharp tip the $\vec{E}$-field is very large $E = \frac{1}{4\pi\varepsilon_0}\frac{q}{r^2}$ $r > r_0$



Choosing the 0 of the electrostatic potential properly, we may write $\phi = Ex$

Then $V(x) = W_A - eEx$ for an electron and with choosing the Fermi edge as the 0 in the potential energy



As the forbidden triangle in the potential energy diagram is only a few Å wide, e^- may tunnel through. The resulting current density is

$$j = A \cdot E^2 \cdot e^{-B\frac{W_A^{3/2}}{E}} \qquad A, B \text{ constants}$$

The electron emission depends therefore sensitively on the local work function. As a sharp tip has many different crystal faces, strong work function contrast is obtained.

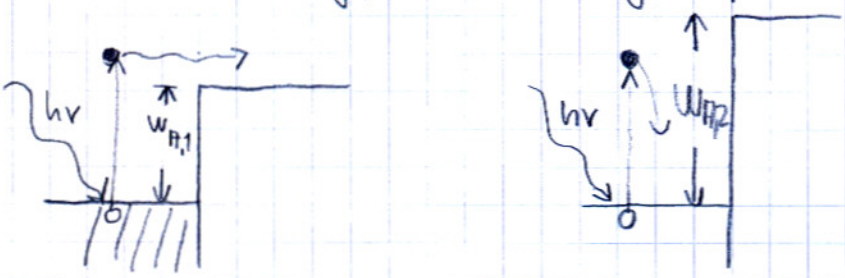
Examples are shown in Figs. 3.15 and 3.16

As the electrons are emitted cold and as the tunneling probability depends strongly on the barrier height, field emitted electrons have a very low energy spread $\approx 0.1\,eV$. As they all stem from a very small area (may be as small as a few nm^2) the electrons are coherent. Field emitters are the basis of most high quality

modern electron microscopies

- (ii) PEEM = photo emission electron microscopy

In its simplest imaging mode, a sample is illuminated with an UV-lamp with photon energy in the range of the work function



Area 1 — photo emission

Area 2 — no photo emission

Depending on the local work function, areas emit photo electrons or they do not. The emitted photo electrons are guided through an electron optical system and form a bright/dark image of the surface. As adsorption, reaction and growth influence the work function, PEEM allows one dynamic growth studies.

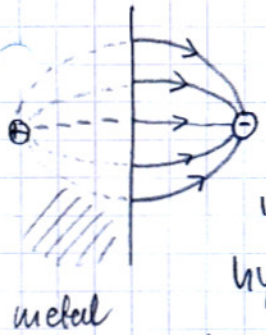
Fig 3.17 shows the outline of an instrument

Fig 3.18 stills from a graphene growth experiment on Ir(111) and a movie is shown.

3.2. Image Potential states

Image potential states are special unoccupied surface states that exist between the Fermi level and the vacuum level of a material. We consider in the following metal surfaces. The material is assumed to have an energy gap around and below the vaccum level. The classical image potential result from the screening of a charge in front of the metal surface.

- The field lines are always ⊥ to the surface, which can be effectively be described by a charge of opposite sign in the metal. The resulting classical image potential is $V(z) = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{4z}$



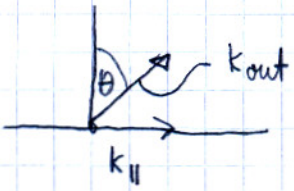
The one dimensional Schrödinger equation for the coordinate along z of an electron in the image potential is precisely identical to the $l=0$ radial part of the hydrogen atom Schrödinger equation with nuclear charge $\frac{1}{4}$. We therefore obtain bound electron states with an energy spectrum of a Rydberg series

$$E_n = -\frac{13.6\,eV}{16\,(n+a)^2}\,, \quad n = 1, 2, \ldots$$

relative to the vaccum energy. The quantity $\underline{a}$ is a quantum correction, taking into a account deviations from the classical image potential inside the metal. Into the metal the wave functions decay exponentially, as usual for a step function of finite height in a 1D potential. Parallel to the surface the electrons behave like free electrons. We therefore obtain the following dispersion relation:

$$E_n = E_{vac} - \frac{13{,}6\,eV}{16\,(n+a)^2} + \frac{\hbar^2 k_\parallel^2}{2m}$$

The parabolic dispersion of image potential electrons can be measured by a 2 photon photo emission experiment, as shown in Fig. 3.19. In such an experiment with a first photon of frequency ω_A an electron from below the Fermi edge is excited and makes a transition to an image potential state. A second photon ω_B releases the electron from the image potential state to the vaccum. The crystal momentum parallel to the surface is conserved in this transition:



$$k_\parallel = k_{out} \cdot \sin\theta \quad \text{with} \quad E_{kin} = \frac{\hbar^2 k_{out}^2}{2m}$$

and energy conservation: $E_n = E_{vac} + E_{kin} - \hbar\omega_B$

allow one to obtain the dispersion relation $E_n(k_\parallel)$ experimentally.

- Fig. 3.20 displays a classical view of the motion of an e^- in front of the surface with $k_\parallel \neq 0$. It performs a hopping motion and bumps periodically against the surface. It can not move into the metal, as there are no states available at these energies. Its decay into an e-h pair (as sketched in Fig. 3.19) is hindered by the small overlap of the image state wavefunction with the wave functions of the solid.

Quantum mechanically a localized e^- is a wavepacket. Such a wave-packet may be formed through the superposition of several image potential - states, which are coherently formed through excitation with a short pulse of finite width in energy (Fig. 3.21). The inset of Fig. 3.21 shows the evolution of the wavepacket with time as a function of its distance from the surface. This evolution is followed by 2 photon photoemission with a variable delay time Δt. The photoemission propability of the wavepacket is only large, when the photon is close to the surface (there the potential gradient provides upon excitation enough momentum for escape). In result, the 2 photon photo emission signal shows a peak structure.

- Electrons in image potential states have a lifetime τ of several ps; compared to e^- in the metal conduction band with lifetimes of ≈ 30 fs the lifetimes of electrons in image potential states are very long. This invites experiments on the electron dynamics in such states.

As you all know from the solid state physics I lecture, an external field $\vec{E}$ causes a shift of the Fermi ball by δk opposite to the field direction:

$$\delta k = \frac{e E \tau}{\hbar}$$

- where τ is the mean scattering time of the electrons. After switching off the field δk relaxes according to $\delta k(t) = \delta k(0)\, e^{-t/\tau}$.

By using a certain trick it is possible to populate an image potential

with a non-equilibrium population of electrons corresponding to a shifted Fermi ball.

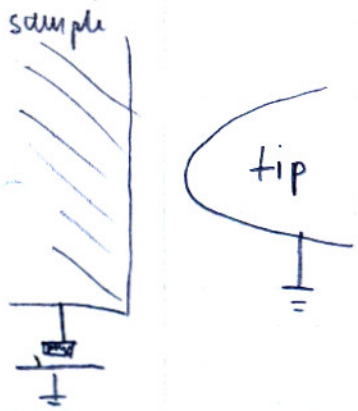
There are now two competing time scales: (i) the depopulation of the image potential state through inelastic electron hole-pair production with a time scale τ_{inel} and (ii) the relaxation of the of nonequilibrium distribution of the electrons through elastic scattering processes at surface defects τ_{el}. Note that this channel includes also processes with phonons, where little energy is changed.

As $\tau_{inel} \gg \tau_{el}$ we are able to see how a non-equilibrium distribution of electrons relaxes to equilibrium. See Figs. 3.22 - 3.24

In conclusion, by clever optical pumping we are able to create electrical current pulses on a surface, which decay by electron elastic or quasi elastic scattering at defects.

There is a second way to measure image potential states. Scanning Tunneling Spectroscopy (STS) is an ideal tool to detect surface states in general and image potential states in particular. From the solid state physics I course you are familiar with STM: a tip is scanned over the sample surface while the tunneling current is kept constant. A plot of the piezo regulation voltage versus tip position yields then essentially the surface topography. There is a second way to use the STM. You put the tip to one location, then open the feedback-loop and measure the tunneling current as a function of voltage.

The experimental situation is like this



and the scematic energy diagram like this