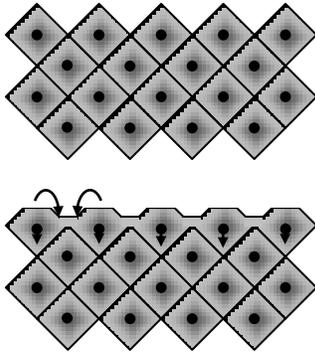


Electronic structure of surfaces

Electronic rearrangement at the surface: relaxations and reconstructions

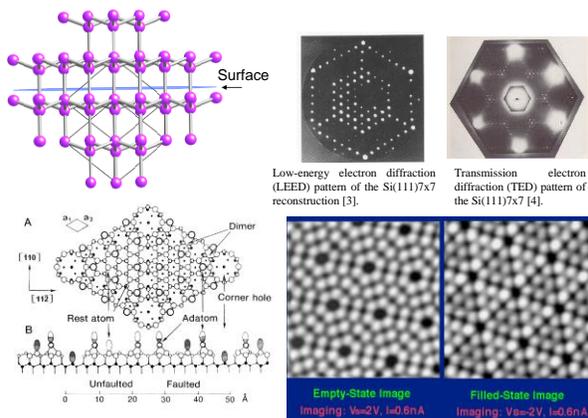


The abrupt termination of a solid at the surface has several consequences on the electronic structure. The electrons rearrange to minimize the surface energy and this rearrangement implies also the rearrangement of the surface atoms. The term relaxation is usually employed to designate the vertical displacement of the first layer of atoms toward the bulk or away from it. This type of restructuring is often observed with metals. The most general case is a contraction of the first interlayer spacing. One can see how this arises by considering a Wigner-Seitz cell with electrons distributed symmetrically around the central ion core. If this electron distribution were maintained at the surface, a strong electronic corrugation would be present.

Energy can be lowered by ‘flattening’ the electronic distribution. This produces an inward displacement of charge that reinforces back-bonding and compensates partially for the broken bonds produced when creating the surface. The displacement of the center of gravity of negative charge causes also the atoms to move inward to minimize their energy by embedding themselves as much as possible in the negative charge cloud. This is the qualitative explanation for the inward relaxation. Most of the observations of the effect were made by LEED, which is specially sensitive to vertical distances in the surface.

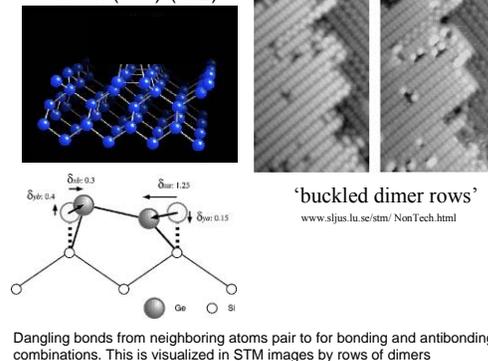
Semiconductors exhibit special reconstructions that are due to the covalent and directional nature of the atomic bonds. The unpaired electrons at the broken bonds in the surface, which are now half-filled, are in a high energy state. Energy is lowered by

Silicon (111): 7x7 reconstruction



3. Schlier, R.E. and Fransworth, H.E., J.Chem.Phys. 30, 917 (1959).
4. Takayangi, K., Tanishiro, Y., Takahashi, S. and Takahashi, M., "Structure analysis of Si(111)-7x7 reconstructed surface by transmission electron diffraction", Surf. Sci. 164, 367 (1985).

Silicon (001)-(1x2)



rehybridization. Atoms undergo substantial displacements to form new bonds. The half-filled orbitals combine to make new filled bonding and empty antibonding orbitals. The resulting surface structure can be quite different from the unreconstructed one. These reconstructions have

been intensively studied because of their importance in semiconductor technology, contacts, surface states, etc. Examples include the Si(111)-(7x7), Si(100)-(2x1) and most other semiconductor surfaces. The subject will be treated separately later on.

Insulators, particularly ionic materials have localized valence orbitals with little sharing of electrons between anions and cations, compared to metals and semiconductors. As a result, surfaces that are electrically neutral, like the (100) planes of alkali halides, are essentially stable and retain their bulk structure. Polar surfaces, like the (111) surfaces that contain one type of ions only are less stable and tend to acquire counterions from the environment, so as to discharge the electric dipole. These surfaces tend to reconstruct.

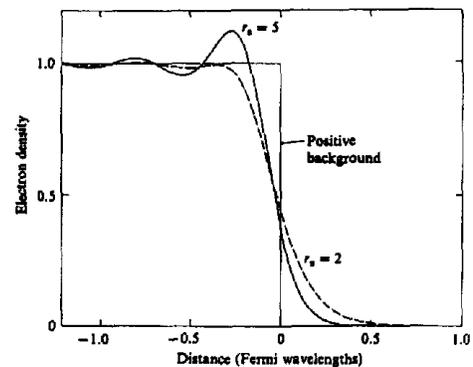
Compounds like oxides present the additional problem of surface stoichiometry. In vacuum environments in particular, it is easy for the surfaces to be oxygen deficient. This is a result of thermodynamics that requires a given pressure of O₂ gas in equilibrium with the oxide. Therefore, in vacuum oxides tend to decompose. The missing oxygen can give rise to altered periodicities, when the vacancies form ordered patterns.

We will now review various aspects of the electronic structure of surfaces. These include the work function, the origin and types of surface electronic states and core level shifts. We will also review the experimental methods to determine electronic structure, both band structure and density of states. The most important techniques for these studies are based on photons.

Work function

The work function of a surface is defined as the minimum energy required to extract an electron from the interior of the crystal to the outside. The potential energy of the positive ion cores holds the electrons bound in the crystal and prevents them from “spilling” out. The electron wavefunctions decay exponentially into the vacuum region, so that they have a small but non-zero density $n(z)$ away from the surface. The excess of electron density outside of the crystal implies a lower charge density inside, for charge conservation. The abrupt termination of the positive charge of the ion cores at the surface can be seen as a perturbation that produces Friedel oscillations, as that shown schematically in the figure. A model used often to calculate these effects is the jellium model. In this model the positive charge of the ion cores is spread out into a smooth constant density of positive charge that is held rigidly in space. The electron density is left free to adopt the distribution that minimizes the energy.

The figure shows the result of such a jellium model for two different densities. Densities are characterized by the radius r_s (in units of the Bohr radius) of the sphere that contains just one electron at the specified density: $n = (4/3 \cdot \pi \cdot r_s^3)^{-1}$. The calculation is from Lang and Kohn (PRB1, 4555(1970)). In addition to the surface dipole due to the charge density oscillations, an important contribution to the work function is due to the image potential. The “extracted electron” produces an image charge of opposite sign that creates a potential equal to $-e/4z$.

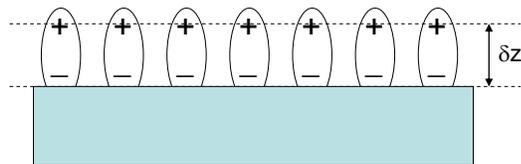


Similar spilling of electronic density and the ensuing oscillations of negative charge occur near other geometrical barriers, as at step edges for example. The electron density is depleted around the corner atom and increased at the bottom of the step. This is called the “Smoluchowski” effect. As a result, a positive dipole, with the positive end pointing out, is associated with step edges. This lowers the work function of step surfaces relative to the flat compact surfaces. The highest work function is found on the most compact surfaces: (111) for fcc, (0001) for hcp, and (110) for bcc.

Work function changes due to adsorbates

Work function of elements, in units of electron volt (eV)			
Ag	4.26 – 4.74	Al	4.06 – 4.26
Au	5.1 – 5.47	B	~4.45
Ba	2.52 – 2.7	Be	4.98
Bi	4.31	C	~5
Ca	2.87	Cd	4.08
Co	5	Cr	4.5
Cs	2.14	Cu	4.53 – 5.10
Fe:	4.67 – 4.81	Ga	4.32
Hg	4.475	In	4.09
Ir	5.00 – 5.67	K	2.29
Li	2.9	Mg	3.66
Mn	4.1	Mo	4.36 – 4.95
Na	2.36	Ni	5.04 – 5.35
Pb	4.25	Pd	5.22 – 5.6
Pt	5.12 – 5.93	Rh	4.98
Ru	4.71	Si	4.60 – 4.85
Sn	4.42	Sr	~2.59
Ta	4.00 – 4.80	Te	4.95
Ti	4.33	U	3.63 – 3.90
V	4.3	W	4.32 – 5.22
Zn	3.63 – 4.9	Zr	4.05

If an adsorbate is present with coverage θ , each molecule or atom having an associate dipole p , due to the chemical bond formed with the substrate atoms or as intrinsic to the molecule, we can view the surfaces as covered by a bilayer of + and – charge separated by δz .

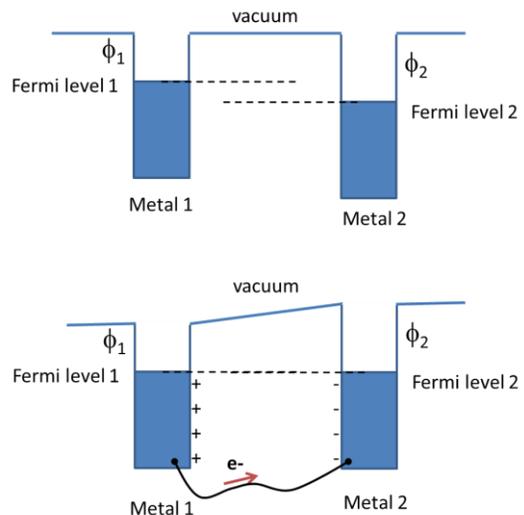


The “field” inside the two surfaces is: $E = \theta \cdot N \cdot e / \epsilon_0$ where N is the surface atomic density e the electron charge and ϵ_0 the dielectric constant and the potential difference, $E \cdot \delta z$, should be the change in work

function. A quick estimation gives values of this change of fractions of 1 eV.

Contact potential

The electric potential between isolated pieces of material is zero (no field). However, if these pieces are joined by a conductive wire the Fermi levels of the materials become equal due to transfer of tiny amounts of charge from the low work function material to the high work function one. This creates an electric field in the space between the materials. The voltage difference is called contact potential.



Exercise: A sphere of Cu of 1 cm radius is connected to a Zinc metal plate. The work functions are: Cu = 5 eV, Zn = 4 eV. When we connect the two with a conducting wire, how much charge is transferred to the Cu?

If evenly spread on the surface, what would be the number of electrons per surface atom?

Measurement of the work function

a) Thermionic emission

One way to determine the value of the work function ϕ is to heat the solid so to thermally excite electrons to energies above the vacuum level. Since work functions are typically a few electron volts, it is clear that the temperature necessary to populate levels at energy ϕ above the Fermi level E_F is rather high ($kT \approx 26$ meV at room temperature). Thermionic emission experiments are carried out at temperatures of a few thousand degrees. At a few eV from E_F the Fermi-Dirac statistics that govern thermal electron energy distributions becomes equal to the classical Boltzmann statistics. If $N(p_z)$ represents the number of electrons with momentum between p_z and $p_z + dp_z$, the number of reaching the surface per unit area and unit time is:

$$\frac{p_z}{m} N(p_z) dp_z \quad (1)$$

The emission current can be found by integration of this quantity for values of p_z between a threshold value p_{z0} and ∞ , where $p_{z0}^2/2m = \phi$:

$$I = \frac{e}{m} \int_{p_{z0}}^{\infty} [1 - r(p_z)] p_z \cdot N(p_z) dp_z \quad (2)$$

We have included a correction for the reflection probability at the surface $r(p_z)$ which is finite even for energies above ϕ . The Boltzmann distribution function $N(p)$ is:

$$N(p_z) = \frac{4\pi mkT}{h^3} \cdot e^{\frac{E_F}{kT}} \cdot e^{-\frac{p_z^2}{2mkT}} \quad (3)$$

Substitution of (3) into (2) and integrating (assuming a constant r) gives:

$$I = \frac{4\pi emkT}{h^3} (1 - r) \cdot T^2 \cdot e^{-\frac{\phi}{kT}} \quad (4)$$

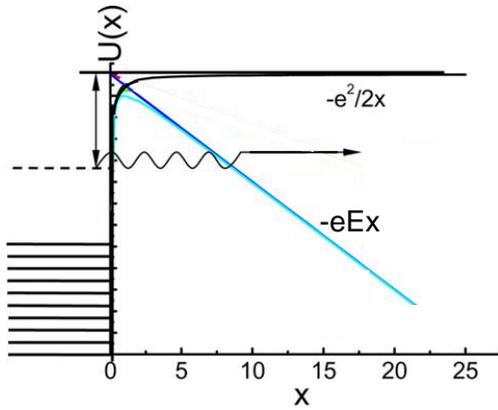
In an experiment one measures I as a function of T . The exponential term dominates expression (4), and so the slope of the line obtained by plotting $\log(I)$ vs $-1/kT$ gives ϕ .

b) Field Emission

Another method of measuring the work function is field emission. In this technique the sample is shaped into a sharp needle that is biased at a high voltage relative to another electrode placed

nearby. For a short radius of curvature at the tip apex the electric field E can be very high, even for moderate voltages because $E = Q/4\pi\epsilon_0 r$,

The potential energy of an electron outside the metal tip is $-e.E.x$, where x is the distance from the tip:



The electrons can tunnel through the roughly triangular potential barrier separating the inside and outside regions. A calculation of this tunneling current leads to the Fowler-Nordheim equation:

$$j = \frac{E^2}{16\pi^2 \hbar \Phi \cdot t(y)^2} \cdot \exp\left(-\frac{4}{3} \sqrt{\frac{2m}{\hbar^2}} \frac{\Phi^{3/2} v(y)}{E}\right)$$

In a semilog plot Φ can be obtained from the slope of $\ln(j/E^2)$ vs $1/E$.

c) The Kelvin method

In this method we measure the current induced in the wire connecting two materials of difference work functions when the distance between the two is varied in a periodic way. The current is due to the change in capacitance and the contact potential difference:

$$Q = C.V = C(z).(\phi_1 - \phi_2)$$

[$= \epsilon S/z.(\phi_1 - \phi_2)$ for a parallel plate capacitor]

Modulating the distance z , for example with a sine wave: $z(t) = z_0 + z_1.\sin(\omega t)$

$$I(t) = \partial Q / \partial t = \partial C / \partial z. z_1.\omega.\cos(\omega t).(\phi_1 - \phi_2) = I_0.\cos(\omega t)$$

The measurement consists in applying a voltage difference between the two such that the current I is zero:

$$I_0 = 0 = \partial C / \partial z. z_1.(\phi_1 - \phi_2 + \Delta V)$$

That gives $\phi_1 - \phi_2 = -\Delta V$

We will later see how this technique can be implemented in an Atomic Force Microscope. In this way we will be able to “map out” the local value of $\phi(x,y)$ with very high spatial resolution (nm).