Tutorial on Work Function

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Work function in metals: Figure 1 shows a schematic energy diagram of a metal. The valence bands are filled with electrons up to the Fermi energy (E_F). The energy difference between Fermi energy and vacuum level corresponds to the work function (Φ). The work function corresponds to the minimum amount of energy needed to remove an electron from the metal. In metals, work function and ionization energy are the same. The work function of a surface is strongly affected by the condition of the surface. The presence of minute amounts of contamination (less than a monolayer of atoms or molecules), or the occurrence of surface reactions (oxidation or similar) can change the work function substantially. Changes of the order of 1 eV are common for metals and semiconductors, depending on the surface condition. These changes are a result of the formation of electric dipoles at the surface, which change the energy an electron needs to leave the sample. Due to the sensitivity of the work function to chemical changes on surfaces, its measurement can give valuable insight into the condition of a given surface. The work function also has significant influence of the band line-up at semiconductor interfaces (see interfaces tutorial).
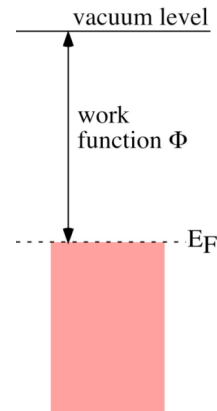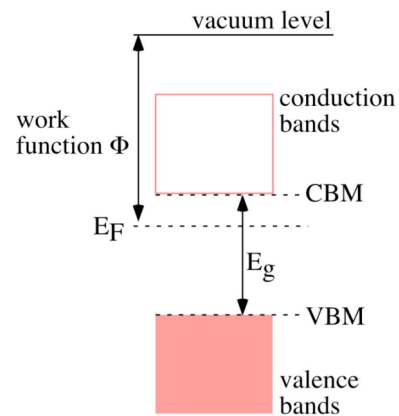
Fig.1: Schematic energy diagram of a metal.

Fig.2: Schematic energy diagram of a semiconductor.

Work function in semiconductors: Figure 2 shows a schematic energy diagram of a n-type semiconductor. Valence bands and conduction bands are separated by the band gap (E_g). In a non-degenerate semiconductor (having a moderate doping level), the Fermi level is located within the band gap. This means the work function is now different from the ionization energy (energy difference between valence bands maximum (VBM) and vacuum level). In a semiconductor, the Fermi level becomes a somewhat theoretical construct since there are no allowed electronic states within the band gap. This means the Fermi distribution needs to be considered, which is a statistical function that gives the probability to find an electron in a given electronic state. The Fermi level refers to the point on the energy scale where the probability is just 50%. Even if there are no electrons right at the Fermi level in a semiconductor, the work function can be measured by photoemission spectroscopy(PES).

Work function measurement techniques: The work function of a material can be measured with PES and Kelvin probe (KP). While PES allows the measurement of the absolute work function, KP only gives the contact potential difference (CPD) between the actual probe and the sample surface. Calibration with PES allows turning KP results into absolute values.

Work function using PES: Figure 3 shows a typical UPS spectrum of a gold sample. The spectrum consists of three features of interest: The spectrum is calibrated in a way that the Fermi level is located at 0 eV binding energy. The Fermi level (or "edge") manifests itself as a step, since it separates occupied and empty states (PES works only with occupied states, since there need to be electrons that can be photoemitted, i.e. states above the Fermi level do not emit electrons). Further to the left at low binding energies (0-10 eV) the valence bands structures of Au are visible. The strong peaks correspond to the d-bands of Au, which have a high density of states and are fairly narrow. Then there is the high binding energy cutoff (or
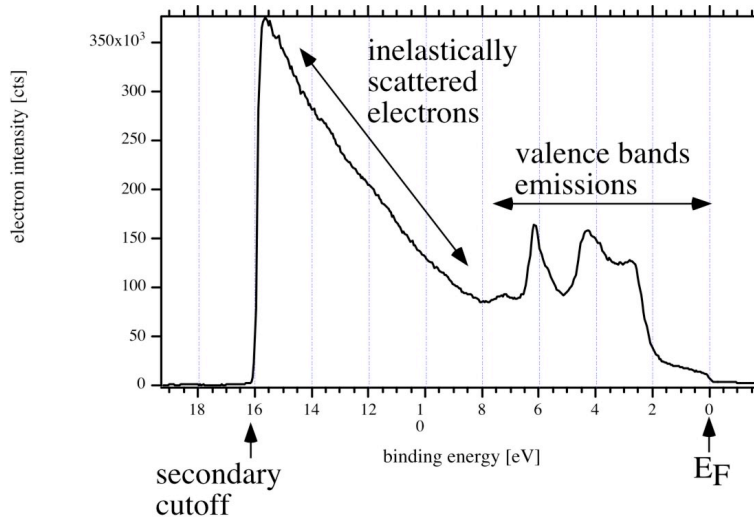

Fig.3: UP-spectrum of Au surface.

"secondary edge"), where the spectrum ends. Electrons close to the edge are the slowest electrons of the spectrum (right at the edge they have a kinetic energy of zero after leaving the sample surface, i.e. they had barely enough energy to overcome the work function of the material). The electrons responsible for the secondary edge and the sloping up tail before the edge are inelastically scattered electrons, which were initially emitted from the valence bands states, but lost energy through scattering processes on their way to the sample surface. Since we know the binding energy of the electrons right at the secondary edge, we can determine the work function, which is just the difference between the energy of the UV photons (21.21 eV for He I radiation) and the binding energy of the secondary edge (15.9 eV in the case of Au). From Figure 3 it follows that the investigated Au surface has a work function of $\Phi_{Au} = 21.21$ eV $-$ 15.9 eV$=$5.3 eV

Work function using KP: For a description of the KP set-up, see the KP tutorial. To measure the work function of a material with KP, a calibration measurement needs to be carried out. The reason for this is that KP can only detect the difference between the work functions of probe and substrate. If KP and UPS are available in the same set-up, a well-defined surface, such as a sputtered Au thin film, can be used to calibrate the KP. In light of the above example on Au, a certain KP contact potential measured relative to the Au surface would be assigned 5.3 eV. Then the unknown sample could be measured using the KP. In

the case of a smaller than Au work function, the KP would yield a negative contact potential, while in the case of a larger than Au work function a positive contact potential would be detected. Hence adding the contact potential to the Au work function value would then yield the actual work function of the sample. In air, it is difficult to obtain an absolute work function measurement with KP since contamination can change the work function of the reference. The best bet, in our opinion is to use highly oriented pyrolytic graphite (HOPG), which after cleavage has a work function of about 4.6 eV. Since HOPG usually does not form interface dipoles, even the presence of typical ambient contamination does not change the work function significantly. This is fundamentally different from metal surfaces where contamination can change the work function by about 0.5-1.0 eV.