Tutorial on Kelvin Probe Measurements

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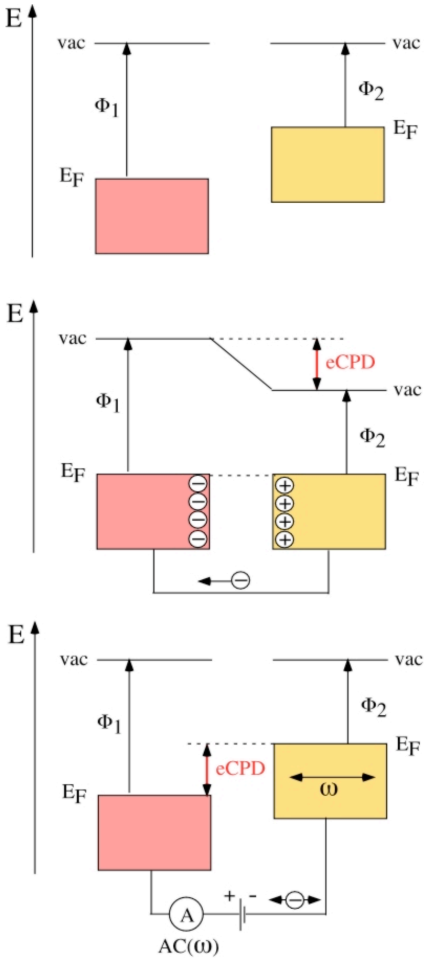

Fig.1: Kelvin probe (KP) measurement process.

The Kelvin probe (KP) technique measures the contact potential difference (CPD) between two surfaces brought in close proximity. Figure 1(top) shows two metals in close proximity, but without electrical contact between them. Their Fermi levels align at the vacuum level at energies corresponding to the respective work functions Φ. As the two metal pieces are connected by a wire (Figure 1 (center)), electrons flow from the metal with the smaller work function to the metal with the larger work function. This causes the smaller work function metal to charge positively while the other charges negatively. This creates an electric potential between the two metals, shifting their electronic states relative to each other. The electron transfer process stops once the electric field between them compensates for the work function difference. In this equilibrated state, the potential associated with the electric field exactly equals the work function difference, i.e. the CPD, between the metals.

This can be utilized for the measurement of the CPD. Gradual application of a counter potential to the CPD and monitoring the charge on one of the metals (for example with an electrometer) allows the determination of the charge-free point. The counter potential V_b that achieves this state is exactly –CPD. In practical instruments one of the metals (the actual Kelvin probe) is vibrated at a certain frequency ω (see Figure 1 (bottom)). Using a lock-in amplifier, the AC(ω) current generated by the oscillation (due to the varying distance, the amount of charge varies that is necessary to maintain the electric field between the surfaces) is monitored. Gradual ramping of the counter potential and finding zero AC current yields CPD. Since small currents are difficult to detect, usually an I/V curve is measured and the I=0 point is found through a curve fit.

Since KP measurements can only detect the CPD, actual work function measurements are only possible through calibration. In other words, the KP needs to be calibrated against a surface with known work function. The challenge in this respect is that under ambient conditions it is challenging to generate a surface with a defined work function. Hence KP measurements are more reliable in vacuum, where a welldefined surface (such as a Ar^+ sputtered Au foil characterized with photoemission spectroscopy, which yields absolute work function values) can more reproducibly be generated and controlled. Under ambient conditions, the use of a highly oriented pyrolytic graphite (HOPG) crystal is probably one of the best methods for calibration. Since HOPG is chemically very inert, it does not form significant interface dipoles with typical ambient contaminants (hydrocarbons, water etc…) found on surfaces. Hence its work function remains fairly stable at about 4.6-4.7 eV.